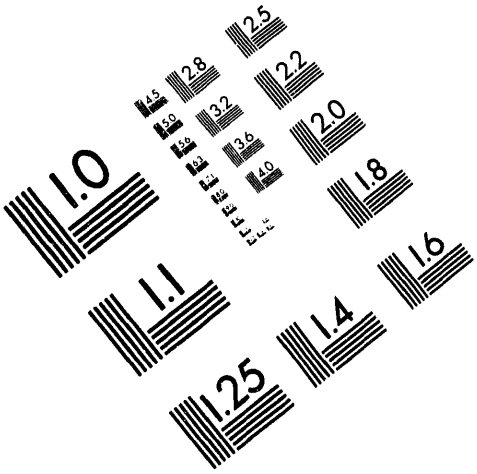

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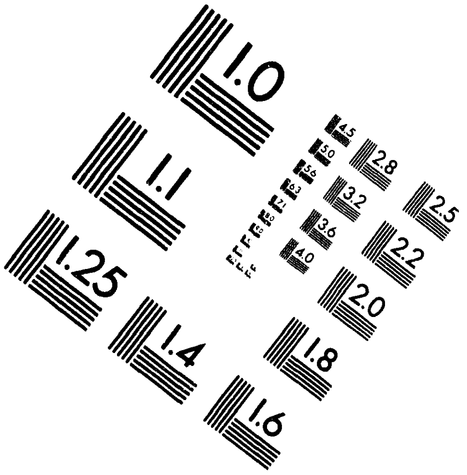

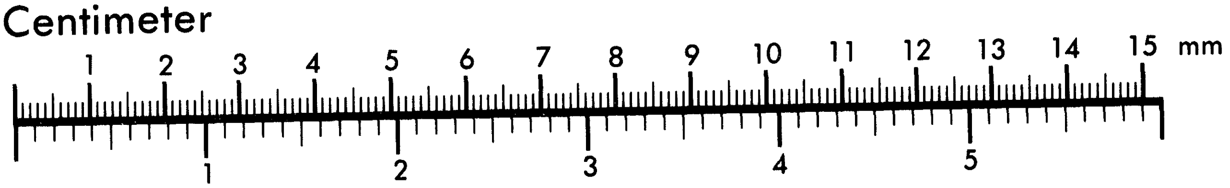

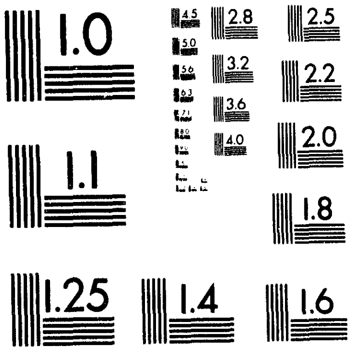

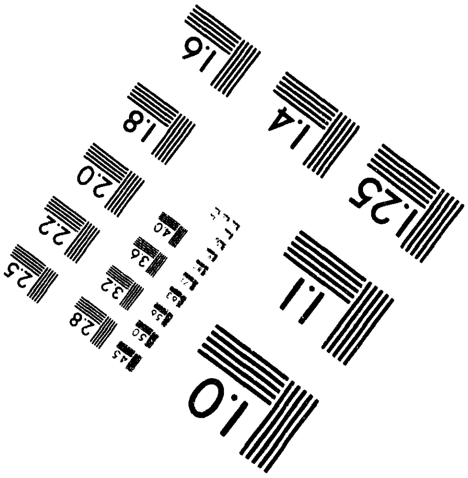

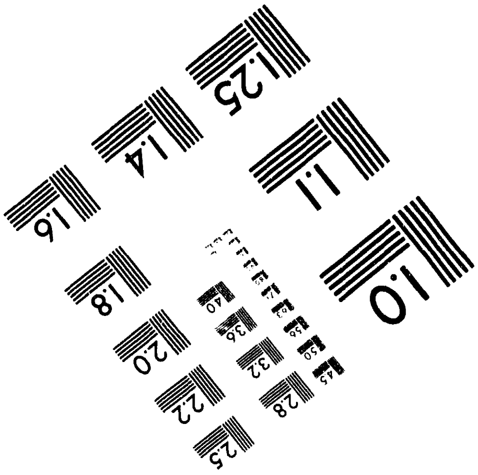

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Preliminary Survey of Separations Technology Applicable to the Pretreatment of Hanford Tank Waste (1992-1993)

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MASTER

Summary

The U.S. Department of Energy has established the Tank Waste Remediation System (TWRS) to manage and dispose of radioactive wastes stored at the Hanford Site. Within this program are evaluations of pretreatment system alternatives through literature reviews. The information in this report was collected as part of this project at Pacific Northwest Laboratory.[a]

A preliminary survey of literature on separations recently entered into the Hanford electronic databases (1992-1993) that have the potential for pretreatment of Hanford tank waste was conducted. Separation processes that can assist in the removal of actinides (uranium, plutonium, americium), lanthanides, barium, ^{137}Cs, ^{90}Sr, ^{129}I, ^{63}Ni, and ^{99}Tc were evaluated. Separation processes of interest were identified through literature searches, journal reviews, and participation in separation technology conferences. This report contains brief descriptions of the potential separation processes, the extent and/or selectivity of the separation, the experimental conditions, and observations. Information was collected on both national and international separation studies to provide a global perspective on recent research efforts.

Separation processes are listed in groups of unit operations under each constituent(s) to be separated. The separations processes described in this text are listed below in Table S.1 with the author(s) and publication year. All these processes are deemed to have potential applicability to the treatment of tank waste.

The processes that are recommended for further study are listed in Table S.2 with some of their positive attributes. These separations processes were selected on the basis that they have recently received attention for application in radioactive environments. The processes of interest include extraction, emulsion-liquid membranes, ion exchange, and ion flotation. These processes offer the potential for good separations, are relatively simple, and do not generate large amounts of secondary waste. The performance of these processes with actual tank waste can only be speculated since a limited amount of information is currently available.

Information compiled in this study has enabled PNL to identify a broad spectrum of recent research efforts that may have potential applications for the pretreatment of Hanford tank waste. However, it was anticipated that many applicable articles would be omitted on a topic as broad as separations. Thus, it was the intent of this report to provide a representative cross-section of recent separations studies. The scope of this study does not provide an exhaustive survey but provides recent information on a broad scale. In part, it is the intent of this review to provide articles from which a more detailed search specific to each technology or constituent can be based. This study builds upon three detailed constituent reviews on cesium, strontium, and transuranic wastes completed during FY93.

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[a] Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

Table S.1. Listing of Separation Processes

	Process	Author(s)	Year
2.1	ACTINIDE SEPARATIONS		
2.1.1	Adsorption - PAA	Grossi, Pietrelli, and Troiuni	1992
2.1.2	Extraction - HEDPA and Sodium Carbonate	Lumetta and Swanson	1993
2.1.3	Extraction - CMPO + TBP	Mathur et al.	1992
2.1.4	Extraction - CMP + TBP	Mathur, Murali, and Natarajan	1991
2.1.5	Extraction - BESO	Shukla and Kedari	1992
2.1.6	Extraction - Picolinamides	Musikas, Cuillerdier, and Coutin	1992
2.1.7	Extraction - Pentaalkylpropanediamide	Cuillerdier, Musikas and Nigond	1992
2.1.8	Extraction - LIX 622	Mohanty et al.	1991
2.1.9	Extraction - Crown Ether and HTTA	Shehata, Khalifa, and Aly	1992
2.1.10	Extraction - HPBI	Manchanda and Mohapatra	1992
2.1.11	Oxidation/Extraction - PMBP and CAAF	Karalova, Lavrinovich and Myasoedov	1992
2.1.12	Oxidation/Extraction - $CsSO_4F$ and Ag(I)	Appelman et al.	1992
2.1.13	Extraction - Alamine-336	Burcik and Mikulaj	1991
2.1.14	Extraction - Microemulsions (AOT/Hexane/CMPO)	Chaiko	1992
2.1.15	Extraction - Aqueous Biphasic (Arsenazo III)	Chaiko et al., Rogers, Bond and Bauer	1993
2.1.16	Emulsion Liquid Membrane - Crown Ether	Shukla et al.	1992
2.1.17	Extraction Chromatography - DAAP (U/TEVA•Spec) Resin	Horwitz et al.	1992
2.1.18	Extraction Chromatography - TRU•Spec and U/TEVA•Spec	Barney and Cowan	1992
2.1.19	Extraction Chromatography - DHDECMP	Schreiber, Dunn, and Yarbro	1992
2.1.20	Extraction - Polyurethane Foams Loaded with HDEHP	Aziz	1992
2.1.21	Extraction - Polyurethane Foam	Huang et al.	1992
2.1.22	Ion Exchange - AG-1x4 Resin	Araujo et al.	1992
2.1.23	Ion Flotation - LPA and PO	Mezhov, Samatov, and Troyanovskiy	1992
2.1.24	Volatilization - Oxygen Flourides and Krypton Diflouride	Kim and Blum	1991

Table S.1. (contd)

	Process	Author(s)	Year
2.2	LANTHANIDE SEPARATIONS		
2.2.1	Extraction - Adogen-464SCN	Borkowski and Siekierski	1992
2.2.2	Extraction - TBP	Ocampo, Gonzales, and Reyes	1991
2.2.3	Extraction - HDEHP	El-Kot	1991
2.2.4	Extraction - Primene JM-T	Jain, Singh, and Tandon	1991
2.2.5	Emulsion Liquid Mebrane - P507	Ho and Li	1992
2.2.6	Ion Exchange - Phosphorous Based Resin (Diphonix)	Alexandratos et al.	1992
2.3	BARIUM SEPARATIONS		
2.3.1	Extraction Chromatography - Crown Ether	Mohite, Jadage, and Pratap	1990
2.3.2	Ion Exchange - Dowex 50W-X8 Exchanger	Husain, Marageh, and Khanchi	1992
2.3.3	Ion Exchange - SuperLig	Camaioni, Colton, and Bruening	1992
2.4	CESIUM SEPARATIONS		
2.4.1	Extraction - Crown Ether + HDDNS	McDowell et al.	1992
2.4.2	Extraction - Crown Ether	Yakshin, Vilkova, and Laskorin	1992
2.4.3	Extraction - Crown Ether	Vibhute and Khopkar	1991
2.4.4	Extraction - Lowinox 22M46	Gulis and Mikulaj	1991
2.4.5	Ion Exchange - Copper Hexacyanoferrate Exchangers	Singh and Ramaswamy	1991
2.4.6	Precipitation - Potassium-Cobalt Hexacyanoferrates	Kent et al.	1993
2.4.7	Precipitation - PTA or NaTPB	Grossi, Pietrelli, and Troiuni	1992
2.4.8	Precipitation - Zinc Hexacyanocobaltate	Mekhail and Benyamin	1991
2.4.9	Recirculating Liquid Membranes - D2EHPA	Blake and Ritchie	1992
2.5	IODINE SEPARATIONS		
2.5.1	Adsorption/Ion Chromatography - Platinum Coated Copper	Lamb et al.	1992
2.5.2	Extraction/Isotope Exchange - TBP and NaI Carrier	Palagyi	1991
2.5.3	Heat Treatment/Air Sparging	Boukis and Henrich	1991
2.6	NICKEL SEPARATIONS		
2.6.1	Extraction - Aliphatic Oxime	Redden and Groves	1993
2.6.2	Flotation - Dissolved Air	Lazaridis et al.	1992
2.6.3	Flotation - Adsorbing Colloid	Sanciolo, Harding, and Mainwaring	1992
2.6.4	Precipitation - Oxalate	Brooks	1993

Table S.1. (contd)

	Process	Author(s)	Year
2.7	STRONTIUM SEPARATIONS		
2.7.1	Adsorption - Polyantimonic Acid	Grossi, Pietrelli, and Troiuni	1992
2.7.2	Extraction - Crown Ether	Horwitz and Dietz	1992
2.7.3	Ion Exchange - Phenolic Exchangers	Samanta, Ramaswamy, and Misra	1992
2.7.4	Emulsion Liquid Membrane - Crown Ether	Mikulaj and Vasekova	1991
2.7.5	Supported Liquid Membrane - Crown Ether	Dozol, Garcia, and Sastre	1991
2.8	TECHNETIUM SEPARATIONS		
2.8.1	Extraction - Crown Ether	Horwitz and Dietz	1992
2.8.2	Extraction - APDC/NaDDC	Chiu, Chu and Weng	1992

Table S.2. Attributes of Promising Separation Processes

Extraction - Pentaalkylpropanediamide
- Easy to synthesize
- Completely incinerable (does not contain phosphorous)
- Potential to separate all actinides
- Extraction from both chloride and nitric acid solutions
- Molecules can be optimized for selectivity

Extraction - Microemulsion (AOT/Hexane/CMPO)
- Able to extract polymeric Pu(IV) (difficult to extract)
- Good $D_{Pu(IV)}$
- Quantitative bulk phase recovery
- Easy to strip
- Silica powder can produce chemically bonded ceramics for waste disposal (good strength and low water permeability)

Extraction - Aqueous Biphasic
- No organic diluent needed
- Preferential partitioning of colloidal particles and complexed radionuclides to polymer rich phase
- Able to extract polymeric Pu(IV)
- Inexpensive, nontoxic, and biodegradable water soluble polymers
- Able to recycle both water soluble polymer and aqueous phase
- Good plutonium separation factors from graphite and SiO_2 mixtures

Oxidation/Extraction
- Separate americium from other trivalent actinides
- Potential to separate americium from lanthanides
- Ambient temperature and pressure process
- Extraction from both acidic and alkaline environments
- Can oxidize Pu(IV) (monomeric and polymeric) to Pu(VI)

Emulsion Liquid Membranes
- Potential for removal of TRUs, rare-earth elements (REE), cesium, and strontium
- Potential for fast kinetics (High interfacial contact area and short contact times)
- Extraction and stripping occur simultaneously
- Simple contactor (i.e., tank)
- In general good, separation factors

Ion Flotation
- Potential for removal of actinides and lanthanides
- Simple contactor
- Simple process

Ion Exchange - Phenolic Exchangers
- Good strontium selectivity
- Good strontium distribution factors
- Good exchange capacity
- No deterioration after gamma irradiation
- Initial fast uptake

Acronyms

alpha (α)	separation factor
AOT	bis(2-ethylhexyl)sulfosuccinate
BESO	bis(2-ethylhexyl)sulfoxide
CAAF	bis(2-oxy-4-alkylbenzoil)amine
CMP	see DHDECMP
CMPO	octyl(phenyl)-N, N-diisobutylcarbamoylmethylphosphine oxide
D	distribution ratio
DA	dodecanoic acid
DOX	decanol oxime
DAAP	diamyl amylphosphonate
DF	Decontaminaton factor
DHDECMP	dihexyl N, N-diethylcarbamoylmethylphosphorate
DOE	Department of Energy
ELM	emulsion liquid membrane
HAW	high active waste
HDEHP	bis(2-etc. or di(2ethylhexyl)phosphoric acid
HEDPA	1-hydroxyethane-1, 1-diphosphonic acid
HF	hydrogen flouride
HLW	high level waste
HPBI	3-phenyl-4-benzoyl-5-isoxazolone
HTTA	thenoyltrifluoroacetone
LLLW	liquid low level waste
LLW	low level waste
LPA	lauril phosphoric acid
MAW	medium active waste
NaTPB	sodium tetraphenylborate
NTIS	National Technical Information Service
ODCB	o-dichlorobenzene
PAA	polyantimonic acid
PCC	platinum-coated copper
PEO	polyethylene oxide
PMBP	1-phenyl-3-methyl-4-benzoylpyrazolone
PNL	Pacific Northwest Laboratory
PO	diphosphine dioxide
PU	polyurethane
POLTOX	Pollution and Toxicology
PPO	phenyl diphosphine dioxide
PTA	phosphotungstic acid
PUREX	plutonium and uranium extraction
REE	rare earth elements
RLM	recirculating liquid membrane
SDS	sodium dodecylsulfate
SLM	supported liquid membrane
TBP	tributyl phosphate

TOPO	tri-n-octyl phosphineoxide
TPO	tolyl diphosphine dioxide
TRU	transuranic

Contents

1.0 Introduction

1.1 Background

Past defense reprocessing and waste management operations at the U.S. Department of Energy's (DOE's) Hanford Site have generated approximately 250,000 m^3 of nuclear waste, which is currently stored in 177 underground tanks. These tanks contain a mixture of sludge, salt cake, and supernatant liquids. The insoluble sludge fraction of the waste consists of metal oxides and hydroxides and contains many of the radionuclides such as the transuranic waste (TRU) components and ^{90}Sr. The salt cake was generated by extensive evaporation of aqueous solutions and consists primarily of dry sodium and potassium salts. The supernatant liquids consist of concentrated (5-15 M) aqueous solutions of sodium and potassium salts. The bulk of water soluble radionuclides such as ^{137}Cs are contained in the salt cake and supernate.

For economic and environmental reasons it is anticipated that the waste will be separated into two fractions for disposal. A high-level waste (HLW) containing the bulk of the radionuclides will be vitrified for final disposal and the low-level waste (LLW) disposed of in a glass form. The separation process is generally termed pretreatment.

Several pretreatment strategies are being considered for pretreatment of the Hanford tank wastes. These strategies range from a minimum pretreatment strategy to an extensive separations strategy. The minimum pretreatment strategy involves sludge washing to remove soluble components and treatment of the supernatant liquids to remove selected radionuclides. The extensive separations strategy involves aggressive dissolution of the sludge followed by separation and concentration of the radionuclides. Radionuclides such as cesium, strontium, technetium, and iodine would also be removed from the supernate.

1.2 Purpose and Scope

The objective of this task was to survey recently published literature on separations that have the potential for pretreatment of Hanford tank waste. Separation processes that can assist in the removal, recovery, and/or destruction of waste constituents of concern were identified. More specifically, processes that could potentially reduce the overall HLW volume by treating waste components that are concerns from a regulatory standpoint and/or for glass and grout disposal.

Separation processes of interest were identified through literature searches, journal reviews, and participation in separation technology conferences. Information was collected on both national and international separation studies to provide a global perspective on recent research efforts. This report contains a brief description of the potential separation processes, the extent and/or selectivity of the separation, the experimental conditions, and observations. The review is not intended to be exhaustive, but to provide a general overview of recent separation work reported in the literature.

1.3 Approach

The selection of articles for review required that important waste components be identified for separation from the Hanford tank wastes. Constituents were identified by being considered a concern from either a regulatory standpoint and/or for glass and grout disposal. The constituents meeting these criteria are well characterized by the "clean option" report (Straalsund et al. 1992) and a review of pretreatment technologies for retrieved single-shell tank waste at Hanford (Gerber 1992). Articles on separation processes were selected by their potential to treat the identified constituents.

Articles of interest were identified through literature searches, journal reviews, and participation in separation technology conferences. This search includes the literature entered into electronic databases from January 1992 to July 1993. Both CD-ROM and online database searches were used. These databases include Government Reports from the National Technical Information Service (NTIS), Enviro/EnergyLine, Pollution and Toxicology (POLTOX), and Energy Science and Technology (formerly Energy Database). Articles published before 1992 have been included in consideration of the time lag between the publication date and entry into the databases.

Initially, a broad title search was conducted for separations and the waste constituents of interest that were entered into the databases after 1991. Unrelated articles were eliminated, and the abstracts of the remaining articles were obtained. Nearly 1000 abstracts were screened, and the number of potentially applicable articles was reduced to nearly 160. Careful screening of the literature produced the articles contained in this review.

This report contains a brief description of the separations process, the extent and/or selectivity of the separation, the experimental conditions, and the general trends observed. It was the intent of this task to provide a broad perspective on current research efforts that may have the potential to treat Hanford tank waste. The complexity, variability, and limited information available on compositions and concentrations within the tanks made a more detailed assessment difficult. In addition, only a very limited amount of literature on processes using Hanford-like solutions is available. Evaluation of the performance of the treatment processes on actual tank waste depends on many factors and often can only be speculated. Therefore, caution must be exercised during extrapolation of limited data to complex situations.

The separation processes are grouped according to the constituents that are the target of separation and then by unit operation. Constituents under consideration include actinides (uranium (U), plutonium (Pu), americium (Am)), lanthanides (chemically similar to actinides), ^{137}Cs, ^{90}Sr, barium, ^{129}I, ^{63}Ni, and ^{99}Tc. Under each constituent, the separations are listed with a heading that provides information regarding the general technology and process characteristics (i.e., Extraction - octylphenyl-N, N-disobutyl carbarmoglmethylphospbine oxide [CMPO] + tributy/phosphate [TBP]). Article objectives and the extent of separation and/or the selectivity of the process are described. Finally, the trends observed with respect to important parameters (concentration, other constituents, pH, etc.) are reported because these factors influence the ability of the separation process to treat specific constituents.

The ability of the process to separate the desired constituent from a waste stream are often reported in terms of a decontamination factor (DF), distribution ratio (D) and separation factor (α). These separation measurements are defined in terms of ratios of activities or concentrations. The DF is given by:

DF = activity or concentration of material initially/activity or concentration of material after treatment

D is given by:

D = activity or concentration of material in organic phase/activity or concentration in aqueous phase.

Separation factors can be defined in terms of a ratio of distribution ratios as:

$\alpha_{D1\text{-}D2}$ = D of 1st constituent/D of 2nd constituent

2.0 Overview of Separations Processes

In the following sections, potential processes for the separation of constituents from Hanford tank waste are discussed. This report contains a brief description of the separation processes, including the extent and/or selectivity of the separation, experimental conditions, and general observations. The separation processes are grouped under the constituents they treat and then by unit operation. Constituents of interest have been identified as actinides (uranium, plutonium, americium), lanthanides, ^{137}Cs, ^{90}Sr, barium, ^{129}I, ^{63}Ni, and ^{99}Tc. Groups of unit operations include extraction, ion exchange, ion floatation, adsorption, chromatography, volatilization, and membrane techniques.

2.1 Actinide Separations

In the Hanford tank waste the important actinides considered for removal are uranium, plutonium, americium, and, possibly, neptunium. These components are primarily found in the sludge fraction of the wastes. Separation of these components from the bulk of the sludge is desirable to reduce the volume of glass that would be produced.

Actinide separations encompass a large area of research emphasis compared to the other constituents under consideration. Recent articles were primarily directed at extraction processes, although ion exchange, flotation, adsorption, volatilization, and membrane techniques were also used.

2.1.1 Adsorption - Polyantimonic Acid

Two flowsheets for the treatment of HLW were considered (Grossi et al. 1992), one based on treatment of the acidic HLW and one based on alkaline HLW. In the acidic HLW flowsheet cesium would be removed by cesium-phosphotungstate precipitation; strontium and plutonium would be removed by polyantimonic acid (PAA) or CMPO sorbed on solid supports. In the alkaline flowsheet, sodium hydroxide would be used to neutralize the HLW to pH > 13, cesium would be removed by sodium tetraphenylborate or zeolite ion exchange, and the strontium and plutonium would be removed with the sludge resulting from the neutralization process. In both flowsheets the separated radionuclides would be vitrified and the LLW would be disposed of in cement. The authors recommended implementation of the alkaline flowsheet using zeolite for cesium removal because good DFs were obtained for all radionuclides; they viewed the process as relatively safe, simple, and reliable; chemicals are readily available for use at the plant scale; and the process has been proven in hot tests and at the pilot scale. However, concerns with long-term performance of the zeolites at pH > 13 have not been addressed. The acidic flowsheet was rejected largely because of the poor performance of the polyantimonic acid (PAA) (i.e., slow kinetics, low DFs, poor mechanical and chemical stability).

2.1.2 Extraction - HEDPA and Sodium Carbonate

Stripping Am(III) and Pu(IV) from TRUEX process solvent (0.2 M CMPO+1.4 M TBP in normal paraffin hydrocarbon) was investigated using 1-Hydroxyethane-1,1-Diphosphonic Acid (HEDPA), and sodium carbonate (Lumetta and Swanson 1993). The solutions were spiked with Am(III) or Pu(IV) tracers. $D_{Am(III)} = 2$ and $D_{Pu(IV)} = 0.5$ were obtained for a 0.01 M HEDPA concentration and 0.35 M HNO_3 concentration. The Ds for both ions decrease with an increasing HEDPA concentration. The lower D for Pu(IV) indicates that this ion can be more readily stripped from TRUEX process solvent with HEDPA than Am(III). In addition, a sodium carbonate strip gave $D_{Am(III)} = 0.001$ and $D_{Pu(IV)} = 0.009$ suggesting that this would be an effective stripping agent. However, during contact of a 0.5 M sodium carbonate strip solution with a TRUEX extract of actual neutralized cladding removal waste, a precipitate rich in lanthanum formed in the strip solution. It was recommended that complexants such as HEDPA be added to prevent precipitation. Experiments that used combined HEDPA/ sodium carbonate as stripping agents were effective and showed that the HEDPA concentration could be reduced from current TRUEX specifications. A sodium carbonate strip offers advantages in that it would eliminate the addition of phosphorus into the HLW stream and that the neutralization of process acids before storage would not be required.

2.1.3 Extraction - CMPO + TBP

The extraction and purification of americium from plutonium loading effluents in 7.5 M HNO_3 solutions has been conducted using 0.2 M CMPO + 1.2 M TBP in dodecane as the extractant (Mathur et al. 1992). Over 97% of the americium (160 mg/L) and over 98% of the plutonium (1.2 mg/L) are extracted in three contacts of five minutes each. Stripping with 0.04 M HNO_3 and 0.05 M $NaNO_2$ recovered approximately 90% of the americium with a plutonium level of 13.2 μg/L. Using an initial extraction at a lower HNO_3 concentration of 4.2 M, one contact with 20% trilaurylamine in dodecane resulted in 97.6% extraction of the plutonium and 2.5% for americium. Following this initial contact with a CMPO+TBP extraction and stripping with 0.04 M HNO_3 + 0.05 M $NaNO_2$ gave >98% americium recovery without detectable amounts of plutonium.

In other related work, the extraction of actinides, lanthanides, and other fission products from high active aqueous raffinate waste (HAW) and HLW solutions generated by the plutonium uranium extraction (PUREX) process was investigated (Mathur et al. 1992). The extractant studied was a mixture of 0.2 M CMPO and 1.2 M TBP in dodecane. The goal of this work was to assess the extraction and stripping behavior of the actinides under actual plant conditions. After four contacts with the extractant the total alpha load in the HLW (3 M HNO_3) was decreased by a factor of 10^3 to about 4 nCi/ml. The Ds were not significantly affected by nitric acid concentrations up to 6 M. Stripping with oxalic acid resulted in recovering all the actinides as a group. Several contacts were required for both the extraction and stripping processes. It was observed that the extraction of the trivalent actinides and plutonium was hindered by the presence of uranium in the feed as it tends to saturate the CMPO in the organic phase. Third phase formation was observed at aqueous feed U(VI) concentrations higher than 9.95 g/L and also with neodymiumAm(III) concentrations higher than 9.2 g/L.

2.1.4 Extraction - CMP + TBP

The extraction of Am(III) from nitric acid solutions (2 - 6 M) was studied using mixtures of dihexyl N,N-diethylcarbamoylmethyl phosphorate (CMP) and TBP in benzene (Mathur et al. 1991). $D_{Am(III)}$ of approximately 7 was obtained for 0.4 M CMP + 0.8 M TBP from a 3.0 M HNO_3 solution. Nearly 99.8% of the Am(III) could be back-extracted by 0.01 M HNO_3. Better extraction was obtained near ambient temperatures and better back extraction at elevated temperatures. In similar experiments mixtures of CMP + TOPO in benzene were used to extract Am(III); however, poor back-extraction significantly limited the recovery.

2.1.5 Extraction - BESO

The extraction of Am(III) from aqueous nitrate media into n-dodecane by bis(2-ethylhexyl)sulfoxide (BESO) was studied (Shukla and Kedari 1992). Sulfoxides are reported to be promising extracting agents, especially for uranium and plutonium; however, the extraction of Am(III) (10^{-6} to 10^{-4} M) was found to be very poor in aqueous nitric acid solutions. A salting-out agent ($Ca(NO_3)_2$) was required to increase the extraction efficiency. The organic phase consisted of 0.4 M BESO in dodecane and an aqueous phase of 0.03 M HNO_3+ (0 to 6 M) $Ca(NO_3)_2$. $D_{Am(III)}$ ranged from <0.01 without a salting-out agent to 163 at a 6 M concentration of $Ca(NO_3)_2$. By increasing the concentration of BESO in the organic phase or calcium nitrate in the aqueous phase the extraction of Am(III) improved. Back extraction of BESO with 1-3 M HNO_3 solution resulted in >99% removal of Am(III). At higher HNO_3 concentrations this extraction process was not as efficient and required a significant amount of salting-out agent.

2.1.6 Extraction - Picolinamides

The preliminary results of a search for extractants that are capable of extracting actinides (III), (IV), and (VI) and while leaving the lanthanides (III) behind are reported in (Musikas et al. 1992). Picolinamides with the formula $C_5H_4NCONRR'$ where R and R' are various substituents have been studied. The highest $D_{Am(III)}$ was 29.8 for $R=H$ and $R'=C_8H_{17}$ in benzene and an aqueous solution of 3 $LiNO_3$. Under similar conditions $D_{Eu(III)} = 3.8$ and an $\alpha_{Am\text{-}Eu}$ of 7.8 was obtained. In aqueous thiocyanic media $\alpha_{Am\text{-}Eu} = 51.5$. Separation factors between americium and praseodymium or neodymium would be more useful as they are much closer to americium in ionic radius than europium. The picolinamides are completely incinerable and were observed to be more selective for trivalent actinides than trivalent lanthanides. Through further modification of the base picolinamides the authors hope to improve selectivity and separation efficiency.

2.1.7 Extraction - Pentaalkylpropanediamide

Pentaalkylpropanediamides were used to complex Am(III) and Pu(IV) in nitric acid and chloride solutions (Cuillerdier et al. 1992). The generic formula is $(RR'NCO)_2CHR''$ where R and R' are alkyl substituents and R" an alkyl or oxyalkyl substituent. The two $C=O$ groups act as chelating agents for metallic cations. For the propanediamides diluted in tertiobutylbenzene, $D_{Am(III)}$ ranged from 1 to 20 for 2 M and 4 M HNO_3 solutions, respectively. In comparison the maximum $D_{Am(III)}$ was 13.7 in a 0.5 M HCl/5.85 M $CaCl_2$ solution. $D_{Pu(IV)} = 60$ was obtained for a 3 M HCl/4.33 M $CaCl_2$ solution. The authors report that they are easy to synthesize and are completely incinerable (do not contain phosphorous). In addition, these chelating agents are reported to be able to separate all actinides even those that are typically difficult with conventional extractants.

In related work the extraction of actinides from chloride medium mixed with concentrated salts was investigated using pentaalkylpropanediamides (Cuillerdier and Musikas 1991). The diamide used for this study was 0.5 M $(C_4H_9CH_3NCO)_2CHC_2H_4OC_6H_{13}$. D_{Am} up to 20 were observed for 3 M HCl and 8 M LiCl in decaline diluent. In a 3 M HCl solution mixed with 10 M LiCl, $D_{Np(IV)} = 224$ and $D_{U(VI)} > 1000$ were obtained. In comparison $D_{Pu} = 578$ was obtained for a monamide extractant in a

5 M HCl solution of several salts. $\alpha_{Am(III)-Pu(IV)}$ > 17000 were achieved. Further optimization of the molecules for greater selectivity is under study.

In concentrated SCN_-, Cl^- (or Br^-) environments, problems can arise due to corrosion, high waste salt production, and, in the case of SCN^-, poor chemical and radiation stability.

2.1.8 Extraction - LIX 622

The extraction of uranium from nitrate media by 10% (v/v) LIX 622 (water insoluble dodecylsalicylaldoxime) in benzene was investigated (Mohanty et al. 1991). At pH 3 no uranium (initial concentration $UO_2 = 5 \times 10^{-3}$ M) extraction occurs, but the extraction increases almost linearly up to pH 6. At pH 6 the extraction efficiency reached 100%. The extraction efficiency increases by increasing LIX 622 concentration, and TBP may be used as a synergist up to 2% by volume. The extraction efficiency decreases with increasing anion concentrations (i.e., Cl, SO_4) and would also be expected to decrease in the presence of sodium.

2.1.9 Extraction - Crown Ether and HTTA

Extraction of trivalent europium, gadolinium, and americium from aqueous perchlorate medium has been studied using mixtures of thenoyltrifluoroacetone (HTTA) and 15-crown-5 (15C5) or 18-crown-6 (18C6) in chloroform (Shehata et al. 1992). Distribution ratio for (Eu(III), Gd(III), and Am(III) were approximately 100 for an organic phase of 0.15 M HTTA and 0.15 M 15C5 in chloroform and an aqueous phase of 0.1 M $NaClO_4$ at pH 3.45. By replacing 0.15 M 18C6 with 15C5, the Ds increased by an order of magnitude to nearly 1000. However, no increase in extraction behavior was observed with the addition of 12C4 over HTTA alone. The highest distribution ratios were obtained at lower hydrogen ion concentrations (10^{-4} M). An increase in the crown ether concentration or the HTTA concentration resulted in an increase of D.

2.1.10 Extraction - HPBI

The extraction of Pu(IV) and Am(III) from acidic medium was investigated using 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) in toluene (Manchanda and Mohapatra 1992). In the range of HPBI concentrations investigated (7.9×10^{-4} M to 2×10^{-3} M), $D_{Pu(IV)}$ ranged from 0.2 to 4. $D_{Am(III)}$ ranged from 1.8 to 15.8 for HPBI concentrations of 3.1×10^{-2} M to 5×10^{-2} M, respectively. In separate experiments, nearly 100% extraction of Pu(IV) was obtained from acidic solutions (HCl, $HClO_4$, H_2SO_4, HNO_3, H_3PO_4) ranging up to 3 N in acid concentration. In the best case, 100% extraction was observed for HNO_3 concentrations up to 5 N.

2.1.11 Oxidation/Extraction - PMBP and CAAF

Using a combination of electrochemical or chemical oxidation and extraction, the separation of americium and curium in solutions of phosphates and sodium carbonate was investigated (Karalova et al. 1992). Initially, Am(III) (10^{-3} M) was electrochemically oxidized to Am(VI) in a 0.1 M solution of $Na_4P_2O_7$ and Cm(III) (10^{-5} M) at pH 10, with an applied potential of 15-19 V for 50 minutes. Extraction of the Am(VI) with a solution of 1-phenyl-3-methyl-4-benzoylpyrazolone (PMBP) in chloroform reduced the Am(VI) to Am(V), which remained in the aqueous phase while Cm(III) was extracted into the organic phase. The $\alpha_{Cm(III)-Am(V)}$ was approximately 1000. The yield of Cm after extraction was 98.4%. In Na_2CO_3 solutions at pH 12.8, Cm(III) will extract quantitatively with bis(2-oxy-4-alkylbenzoil)amine (CAAF), while the Am(III) previously oxidized to Am(VI) remains in the aqueous phase. It is expected this method could be used for separation of Am(III) from Cf(III), Bk(III) and trivalent REE as they extract similarly to Cm(III) under these conditions.

2.1.12 Oxidation/Extraction - $CsSO_4F$ and Ag(I)

The separation of americium from curium was investigated using cesium flouroxysulfate ($CsSO_4F$) with Ag(I) catalyst to rapidly oxidize Am(III) to Am(VI) followed by extraction (Appelman et al. 1991). Initial concentrations were 7.5×10^{-3} M Am(III) and 7.5×10^{-5} M Cm(III). This process was performed at ambient temperature in 0.4 to 1.0 M HNO_3 where fluoroxysulfate reacts with Ag(I) to produce higher oxidation states of silver which in turn oxidizes the Am(III) to Am(VI). After oxidation, bis(2,6-dimethyl-4-heptyl) phosphoric acid diluted in dodecane is used to extract the Am(VI) from the Curium(III). DF_{Am} of 4000 and DF_{Cm} of 280 were obtained for the process. The oxidation of Am(III) to Am(VI) becomes much slower once the solution reaches 2.6 M in HNO_3. The authors report concerns with the build-up of HF as the oxidant decomposes, which could precipitate trivalent or tetravalent actinide ions. Also the presence of silver catalyst creates additional waste disposal concerns.

2.1.13 Extraction - Alamine-336

The separation of thorium, uranium, and plutonium was investigated using Alamine-336 and tri-n-octylphosphineoxide (TOPO) in xylene or cyclochexane (Burcik and Mikulaj 1991). This work was directed at the development of an analytical method for the determination of thorium, uranium, and plutonium. Using 20% Alamine-336 in xylene $D_{Pu(IV)}$ was as high as 300 in 1 M HNO_3 solutions. A maximum $D_{U(VI)}$ of 25 was obtained in a 3 M HCl solution. Higher Ds were obtained with TOPO (D_{Pu}(IV) = 500, $D_{U(VI)}$ = 1000), but complete back extraction was much more difficult than with Alamine-336. In the presence of Ca(II), Fe(III), and Mn(II), the recovery efficiency for thorium, uranium, and plutonium was significantly reduced. It was concluded that the method was only suitable for analysis of samples with low concentrations of interfering ions.

2.1.14 Extraction - Microemulsions (AOT/Hexane/CMPO)

Extraction of colloidal Pu(IV) by microemulsion-based solvent extraction systems was investigated using microemulsions that consist of the surfactant sodium bis(2-ethylhexyl)sulfosuccinate (AOT) in hexane with either CMPO, or TBP as coextractant (Chaiko 1992). A D_{Pu} value of 3000 was obtained at 0.4 M HNO_3 in the aqueous phase and at 0.2 M CMPO and 0.15 M AOT in hexane for the organic phase. The D_{Pu} for the system using TBP/AOT in hexane were considerably lower. The extraction kinetics of the CMPO/AOT system was considerably faster than the TBP/AOT system. The bulk phase recovery of plutonium was 100% for both organic extractants. After partitioning of the plutonium, back-extraction of plutonium was accomplished by encapsulation of the extracted metal species in colloidal silica particles that were produced by the acid-catalyzed hydrolysis and polymerization of tetraethoxysilane within the aqueous microdroplets of the organic phase. The SiO_2 capsules were precipitated from the organic phase by increasing the pH with hydrazine or ammonium hydroxide. The water soluble polymers used for biphase formation are nontoxic, biodegradable, and relatively inexpensive.

2.1.15 Extraction - Aqueous Biphasic (Arsenazo III)

An aqueous biphasic system is a heterogeneous liquid/liquid system that spontaneously forms in mixtures of two dissimilar water soluble polymers or of a water soluble polymer and an inorganic salt. Colloidal-size particles and certain complexed radionuclides have been shown to preferentially partition to the polymer rich phase. The process can be considered similar to conventional solvent extraction except that an organic diluent is not used. Contactors similar to those currently in use for conventional solvent extraction can probably be used.

Initial experiments were conducted to determine the feasibility of using aqueous biphasic extraction systems for separation and recovery of plutonium from aqueous waste streams or solids residues (Chaiko et al. 1992, 1993). The initial target of these experiments was PuO_2 contained in solid residues (e.g., incinerator ash, sand, slag, and crucibles; graphite). However, the authors used polymeric Pu(IV) as a stand-in for PuO_2. Polymeric Pu(IV) was extracted using the sodium sulfate/polyethylene glycol system and the phase transfer agent (PTA) arsenazo III. Single stage separation factors of 10^4 and 10^6 were obtained for plutonium/graphite and Pu/SiO_2 mixtures, respectively. The authors speculate that the surface properties of plutonium polymer and PuO_2 particles are similar (both contain hydrated Pu-OH sites) and are attempting to correlate the partitioning behavior.

In a related study polyethylene glycol (PEG) was added to $(NH_4)_2SO_4$ and K_2CO_3 for use in extracting Am(III), Pu(IV), UO_2(II), and Th(IV) into the polymer rich phase from a salt rich phase (Rogers et al. 1993). Complexing dyes were used to preferentially partition to the polymer rich phase. Dyes used include arsenazo III, alizarin complexone, and xylenol orange. In SO_4^{2-} media, at an arsenazo III concentration of 10^{-4} M, Ds greater than 10 for Th(IV), UO_2(II), and Pu(IV) were obtained. At higher arsenazo III concentrations (1.5×10^{-3} M), $D_{Am} > 10$. However, in CO_3^{2-} media arsenazo III exhibited poor extraction capabilities. For the alizarin complexone dye, concentrations of 10^{-4} M to 10^{-5} M were necessary to achieve Ds > 10 for plutonium and thorium in SO_4^{2-} media. In CO_3 media the Ds were > 10 for an alizarin complexone concentration of 0.01 M. In comparison, for xylenol orange concentrations between 10^{-5} M and 0.05 M, Ds were > 10 for thorium and americium (as high as 1000 for D_{Am}) in SO_4^{2-} media. D_{Pu} was > 10 between 3×10^{-6} M and 0.05 M xylenol orange concentration. In the CO_3^{2-} media, only D_{Am} was > 10 at xylenol orange concentrations $> 3 \times 10^{-3}$. The Ds in the absence of complexant were significantly less than 1 indicating that the complexant is necessary for a viable process. The Ds indicate that stripping could be accomplished with 3 M H_2SO_4 ; however, no stripping experiments were carried out. Other water soluble complexing agents are being investigated as many complexing dyes are expensive and toxic. The partitioning behavior of strontium was not investigated.

2.1.16 Emulsion Liquid Membrane - Crown Ether

Plutonium was removed from nitric acid streams by an emulsion liquid membrane (ELM) process using dicyclohexano18-crown-6 (DC18C6) as the extractant diluted in toluene or paraffin (Shukla and Kedari 1992 in Ho and Li 1992). The membrane phase is interposed between the continuous external phase and an encapsulated internal phase. The membrane phase consisted of 0.2 M DC18C6, with polyamine or SPAN-80 surfactants in toluene diluent. The internal phase was 0.5 M Na_2CO_3. More than 90% of the plutonium (50 mg/l) was removed from a 3 M nitric acid/0.05 M sodium nitrate feed stream. It was suggested that higher separations would be achievable by determination of appropriate surfactants. Concerns with the stability of the ELM, especially in nitric acid environments, need to be addressed.

2.1.17 Extraction Chromatography - DAAP (U/TEVA•Spec) Resin

A new extraction chromatographic resin consisting of diamyl amylphosphonate (DAAP) sorbed on an inert polymeric support (Amberlite XAD-7) was investigated for the separation of uranium from nitric and hydrochloric acid solutions (Horwitz et al. 1992). This material is commercially available as U/TEVA•Spec (uranium and tetravalent actinide specific). Based on the capacity factor, k' (number of free column volumes to peak maximum) the U/TEVA•Spec resin shows that the resin will effectively sorb uranium over a wide range of nitric acid concentrations ($>$ 1 M - 10 M). At low acid concentrations (0.02 M) the uranium can be easily stripped. Due to the differences in k' between uranium and thorium, separation of the ions can be achieved through proper selection of the stripping solution acid concentration. During tests on environmental samples (e.g., groundwater and sediment) over 95% recovery of uranium was achieved. As only dilute acid is required for elution, a reduction in reagent consumption and secondary waste generation is possible. However, for application to Hanford tank wastes a significant amount of reagent would be required for pH adjustment.

2.1.18 Extraction Chromatography - TRU•Spec and U/TEVA•Spec

Extraction chromatographic resins were evaluated as an alternative to using the TRUEX process for separation of americium, plutonium, and uranium from acidified Hanford tank wastes (Barney and Cowan 1992). A laboratory prepared resin (CMPO loaded on macroporous support of Amberlite XAD-16), two commercially available resins TRU•Spec (CMPO+TBP on macroporous polymeric support), and U/TEVA•Spec (Dipentyl Pentylphosphonate on macroporous polymeric support) were used for the separations. DF_{Am} as high as 42,000 (initial ^{241}Am activity 0.089 μCi/ml) was observed at lower acid concentrations, and DF_U as high as 2600 (initial ^{232}U activity 0.02 μCi/ml) were obtained. DF_{Pu} = 67,000 (initial ^{238}Pu activity 0.017 μCi/ml) was measured for a 0.5 M HNO_3 solution. Actinide extraction is decreased by the presence of metal ions that compete for the CMPO complexant. Nitrate ion increases extraction of the actinides due to nitrate complex formation, while acid concentration decreases extraction because of competition for the CMPO extractant. Extraction with TRU•Spec resin is rapid, and elution is easily achieved with ammonium citrate. The laboratory prepared resin showed promising extraction properties similar to the TRU•Spec resin. It was concluded that both of the materials could be used to remove actinides from acidified Hanford tank wastes.

2.1.19 Extraction Chromatography - DHDECMP

The results of a laboratory and engineering evaluation of technologies for a secondary unit for cleanup of effluent from a plutonium anion exchange recovery operation are reported in (Schreiber et al. 1992). Initially, liquid/liquid extraction was investigated using 30% by vol. DHDECMP in diisopropylbenzene as the extractant in modified York-Scheibel columns. Lean-residue anion-exchange column effluent used for the feed was between 4 and 8 M in HNO_3 and contained 100 mg/L plutonium and 10 mg/L americium. Over 95% of the plutonium and americium was removed and recovered. However, this process was rejected because the authors felt that the process was difficult to operate effectively on a pilot scale and would require extensive process control to operate on a plant scale. To improve the recovery, the extractants were loaded on, or incorporated in, a resin for extraction chromatography. Distribution coefficients for plutonium ranged from 11.8 to 140 and for americium 0.7 to 49, depending on the swelling solvent (toluene, chloroform, and methylene chloride), bead structure (styrene-divinylbenzene, polyacrylate), and extractant (CMPO, DHDECMP). A reduction in activity by 99.999% was observed. However, breakthrough occurred after only 3 bed volumes of effluent contacted. Thus, the effective loading was only 10 mg of actinides per liter of resin. The authors report that the extractants are difficult to synthesize in high purity, difficult to back extract, and would cause formation of phosphates and pyrophosphate in ash during thermal disposal. These concerns led the authors to investigate malonamides for extraction of trivalent, tetravalent, and hexavalent actinides from nitric acid solutions. Initial studies have obtained D_{Pu} that range from 0.3 to 175 for 0.1 M to 7.0 M HNO_3 concentrations, respectively, for nitrogen, N-dimethyldibutylmalonamide in diisopropylbenzene and 10% octanol solution.

2.1.20 Extraction - HDEHP Loaded Polyurethane Foams

The use of polyurethane foams for immobilizing organic extractants was investigated for the enrichment of metal ions from aqueous media. Solutions of di(2ethylhexyl)phosphoric acid (HDEHP) in o-dichlorobenzene (ODCB) immobilized in polyurethane foam were used to extract U(VI) (2.5 x 10-3 M) from nitric acid solutions (Aziz et al. 1992). Concentrations of HDEHP in ODCB were varied from 0.04 mmol to 0.05 mmol. A maximum D_U of 11,500 was obtained for conditions of 0.1 M HNO_3 and 0.4 mmol HDEHP in ODCB. At 3.5 M HNO_3 and 0.05 mmol HDEHP in ODCB, the D_U dropped to 12. Nitric acid and HDEHP concentrations had a strong influence on D_U. Nitric acid concentrations had to be kept below 3.5 M as higher concentrations are destructive to the polyurethane foam. Large quantities of this material subject to poor heat transfer could lead to exothermic and runaway reactions (i.e., explosions in a relatively closed experiment).

2.1.21 Extraction - Polyurethane Foam

The extraction of U(VI) from aqueous solution with polyether based polyurethane (PU) foam was investigated (Huang et al. 1992). Experiments were carried out in nitrate solutions containing 0.06 M HNO_3 and 2.1×10^{-3} M U(VI). The polyurethane foam was unable to extract any uranium without a nitrate salting-out agent. With the addition of 10 N $Ca(NO_3)_2$, a $D_{U(VI)} = 1286$ was obtained for the polyurethane foam containing 12% polyethylene oxide (PEO). Lower PEO contents in the foam always showed a decrease in $D_{U(VI)}$. D_U increases at lower temperatures and lower nitric acid concentrations.

2.1.22 Ion Exchange - AG-1x4 Exchanger

Recovery of trace levels of plutonium from uranium solutions was investigated using an ion exchange technique (Araujo et al. 1992). Plutonium nitrate solutions were passed through a chromatographic column filled with AG-1x4 anionic resin. The plutonium was eluted with 0.4 M HNO_3. The plutonium breakthrough point corresponded to 3.25 mg plutonium/ml resin. The presence of uranium did not interfere with plutonium retention on the resin at low uranium/plutonium ratios. At higher uranium/plutonium ratios (10^4) the uranium interfered with plutonium sorption. Unfortunately, the authors do not report their results for plutonium breakthrough as a function of initial plutonium or uranium/plutonium. A decrease in resin capacity would be expected with a decrease in plutonium concentration. In addition, at high uranium concentrations the competition between uranium and plutonium and lower absorption kinetics are expected to reduce the resin capacity.

2.1.23 Ion Flotation - LPA and PO

The feasibility of ion flotation of europium and americium from nitric acid solutions using lauril phosphoric acid (LPA) or diphosphine dioxides (PO) was investigated (Mezhov et al. 1992). These floto-reagents form a barely soluble hydrophobic precipitate from chemical interaction with metal ions. Passing air through the solution concentrates the metal ion-floto reagent in a thin layer of unstable foam that can be easily separated from the bulk solution. Over 97% europium (initial concentration 3.2×10^{-4} M) removal was achieved at low HNO_3 concentrations (0.1-0.7 M) with 0.3% LPA in 2 M NH_4OH. For higher acid concentrations phenyl diphosphine dioxides (PPO) and tolyl diphosphine dioxides (TPO) were used as the floto-reagent. For 0.02 M PPO in ethanol, 38% of the americium (initial concentration 2.1×10^{-7} M) was removed at a 4.2 M HNO_3 concentration per one flotation operation. Compared to 0.02 M TPO in ethanol, the amount of americium removed per operation varied from 48% at 4.2 M HNO_3 up to a maximum of 76% at 3.1 M HNO_3, indicating that TPO is a more effective agent. Under similar conditions better removal efficiencies were always obtained for Pu(IV). In all instances the extent of metal removal increased with an increase in floto-reagent expenditure.

2.1.24 Volatilization - Oxygen Flourides and Krypton Diflouride

Oxygen flourides and krypton diflouride are used to volatilize plutonium compounds to PuF_6, which can be easily separated from the gaseous product stream (Kim and Blum 1991). The recovered plutonium has a chemical purity that eliminates further purification steps. Incinerator ash from a nuclear processing plant was contacted with the flouride compounds, reducing the plutonium content by 60%. The authors expect to improve on these preliminary results through process optimization. The authors are working to resolve the concern that oxygen flouride and krypton diflouride are thermally unstable, which make production and storage of large quantities of the reagents difficult.

2.2 Lanthanide Separations

The lanthanides may warrant separation because they would contribute a significant mass to the HLW volume if an extensive separations strategy is pursued. The chemical similarities with the TRU components (especially americium) make clean separations difficult. Reduction of the HLW volume would warrant some lanthanide separations. Recent studies involving lanthanide separation processes include extraction, ion exchange, and emulsion liquid membranes.

2.2.1 Extraction - Adogen-464SCN

The extraction of lanthanum, europium, lutetium, yttrium, americium, and californium by Adogen-464SCN from ammonium thiocyanate solutions was studied as a function of thiocyanate concentration (Borkowski and Siekierski 1992). In the range of thiocyanate concentrations investigated (0-4 M), the distribution ratios initially increase rapidly up to 0.25 M followed by a slower increase up to the 4 M ammonium thiocyanate concentration. $D_{La} = 0.8$, $D_{Eu} = 4.5$, $D_{Lu} = 100$, $D_{Am} = 70$, $D_{Cf} = 30$, and $D_Y = 2.5$ were obtained for 0.11 M Adogen-464SCN in xylene. The degree of complex formation in the aqueous phase decreases across the lanthanide series and increases between americium and californium, whereas in the organic phase it increases for both series.

2.2.2 Extraction - TBP

The solvent extraction and chromatographic elution of cerium, praseodymium, neodymium, samarium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium were investigated (Sanchez-Ocampo et al. 1991). TBP was used to extract uranium (initial concentration 0.5 M) from the REE (initial concentrations 0.005 M) at various HCl concentrations. D_U of approximately 90 was obtained for 5-9 M HCl concentrations, while D_{REE} of 0.006 was observed. Only lutetium was appreciably extracted into the organic phase. This solution was sent to a column containing Dowex 50W-x8 resin. Quantitative elution was obtained for uranium with 0.75 M H_2SO_4, followed by elution of each of REE with 5,6, or 7 M HCl and cerium lone with 4 M HCl. The separation coefficient for uranyl/REE was 15000.

2.2.3 Extraction - HDEHP

Using bis (2-ethylhexyl) phosphoric acid (HDEHP) the extraction of Ce(III) from U(VI) and Th(IV) in hydrochloric and sulfuric acid solutions was studied (El-Kot 1991). The addition of water-miscible alcohols or acetone to the aqueous phase increased the separation efficiency. Separation factors for uranium from cesium were near 450 were obtained with 20% HDEHP in benzene for 2.5 M HCl in the presence of acetone. Under similar conditions $\alpha_{Th\text{-}Ce}$ were near 1000. In the case of thorium even higher separation factors were obtained for mixed acid solutions of HCl and H_2SO_4. The separation factor increases with increasing acid concentration, passes through a maximum, and then decreases.

2.2.4 Extraction - Primene JM-T

In a development effort aimed at separating lanthanides from Ti(IV), Zr(IV), Th(IV), and U(VI), an amine, Primene JM-T was used to extract lanthanides and other associated elements from citric acid medium (Jain et al. 1991). The citric acid concentration was varied from 1.0 x 10^{-3} M to 5.0 x 10^{-3} M while the organic phase consisted of 3% Primene JM-T in chloroform. Between 90% and 100% extraction was obtained for Ti(IV), V(IV), Th(IV), and U(VI) (initial metal ion concentration 1.0 x 10^{-4} M), while greater than 95% of the Ce(III), Gd(III), and Yb(III) remained in the aqueous phase. Titanium, zirconium, and uranium could be recovered quantitatively from the organic phase by washing with 6 M HCl and the thorium recovered with 3 M H_2SO_4. Increasing Primene JM-T concentration resulted in a reduction of the extraction efficiency.

2.2.5 Emulsion Liquid Membrane - P507

Rare earth metals were extracted by ELMs from dilute solutions (Li and Xu, in Ho and Li 1992).[a] The membrane phase consisted of mono(2-ethylhexyl) 2 -ethylhexyl-phosphonate(P507) (3.5 vol. %), with the surfactant N113A (4.5 vol. %) in kerosene (88 vol. %) and paraffin (4 vol. %). The internal phase was 2 M HCl. Between 94% and 100% removal of La(III) (0.2-0.8 mg/L) was obtained from a 0.1 M HOAc/0.1 M NaOAc feed. Other lanthanides such as Eu(III) and Lu(III) have been removed with >99% efficiency using ELMs.

(a) Li, Y.-T, and S.-S. Xu. 1991. "Lihua Jianyan". *Huaxuc Fence*, 27:270 (in Chinese).

2.2.6 Ion Exchange - Phosphorous-Based Exchanger

A relatively new ion exchange resin with diphosphonic acid ligands displays metal ion selectivity and rapid rates of complexation over a wide solution pH range (Alexandratos et al. 1992). This material is referred to as Diphonix, a commercially available resin (from Eichrom Industries Inc.) that was able to complex 98.3% of Eu(III) from 1 N HNO_3 solutions after a 30 minute contact. In the presence of sodium the Diphonix resin was still able to complex 96.5% of the Eu(III) from a 1 N HNO_3/0.4 N $NaNO_3$ solution. Diphonix also showed better selectivity than sulfonic acid and iminodiacetic acid ligands for metals such as nickel, zinc, lead, and mercury. Unfortunately, the authors do not provide information regarding the distribution coefficient, which would enable a much better assessment of these resins.

2.3 Barium Separations

Chemical similarities between barium and strontium make their separation very difficult. For strontium to be disposed of in the lowest volume of glass possible it may be necessary to separate it from barium. Recently, only a few efforts using ion exchange methods were directed toward barium/strontium separations as most barium separations are associated with the superconductor industry.

2.3.1 Extraction Chromatography - Crown Ether

An extraction chromatographic separation of barium from a picric acid solution was conducted using dibenzo-18-crown-6 coated on hydrophobic silica gel (Mohite et al. 1990). In a ternary mixture containing barium (initial 0.25 mg), strontium (initial 7.0 mg), and a metal ion such as calcium (initial 10 mg) with 0.01 M picric acid, the barium and strontium were coextracted while the other elements passed through the column. In the binary mixture the strontium was first eluted with water and the barium was stripped with 2 M HNO_3. Quantitative recovery of all the elements was observed. Barium was also removed from solutions containing alkali metals, uranium, and thorium.

2.3.2 Ion Exchange - Dowex 50W-X8 Exchanger

The separation of Ba(II) from Sr(II) was reported by using Dowex 50W-X8 resin and eluting with a formic acid-methyl ethyl ketone-methanol solution (Husain et al. 1992). Using the differences in distribution coefficients defined as

$$\left[\frac{\mu\text{g of element/g of resin}}{\mu\text{g of element/ml of solution}}\right]$$

for barium (25) and strontium (< 1.0) in 0.1 M formic acid/3 M sodium formate/50% methanol solutions 2.212 mg of strontium were separated from 3.468 mg of barium. During elution with 0.1 M formic acid/3 M sodium formate/50% methanol, the strontium appears first and barium appears in the later fractions. Additional information regarding D for 45 other elements were determined at various formic acid/MEK/methanol solvent concentrations.

2.3.3 Ion Exchange - SuperLig Exchanger

The selectivity of separation of metal ions from synthetic nonradioactive waste was investigated using the commercially available silica-bonded macrocyclic ligand, SuperLig (Camaioni et al. 1992). The PUREX raffinate simulant feed contained approximately 1.1 mmol Ba(II) and 0.8 mmol Sr(II). Strontium elution was carried out by adding 0.1 M Na_3citrate, and barium was eluted with 0.03 M Na_4EDTA. In a column containing 10 g of SuperLig, between 90% and 98% of the Ba(II) and 73% to 86% of the Sr(II) were separated from the test solution. Problems with premature breakthrough were attributed to inefficient packing of the column and channeling. Other separations investigated with SuperLig included cesium and rubidium, palladium, and ruthenium and argentum.

2.4 Cesium Separations

Cesium-137 is a highly radioactive beta emitter and a significant contributor to the overall activity in the Hanford tank waste. The high activity makes it necessary to remove the ^{137}Cs to ensure that the LLW meet the lowest possible limits. Recent research efforts on cesium separations include precipitation, recirculating liquid membranes, ion exchange, and extraction processes.

2.4.1 Extraction - Crown Ether + HDDNS

The extraction behavior of bis[4(6)-tert-butylbenzo]-21-crown-7 (D(tBB)21C7) in a toluene solution with didodecylnaphthalenesulfonic acid (HDDNS) for the separation of cesium from nitric acid solutions was investigated (McDowell et al. 1992). Under nonloading conditions for 0.25 M HDDNS and 0.25 M (D(tBB)21C7) in toluene with an aqueous phase of 0.1 M in nitric acid, D_{Cs} was 100 and the $\alpha_{Cs\text{-}Na} = 294$. Under competitive extraction conditions, the $D_{Cs} = 5$ and the $\alpha_{Cs\text{-}Na} = 192$. Increasing the concentration of D(tBB)21C7 and HDDNS or reducing the acid concentration increases D_{Cs}.

2.4.2 Extraction - Crown Ether

Several crown ethers were studied for separating cesium from picric acid solutions (Vibhute and Khopkar 1991). DB-24-crown-8 in dichloromethane showed the best extraction capabilities at a picric acid concentration of 0.01 M and pH 3. Essentially 100% extraction of cesium (initial concentration 25 μg) was observed for crown ether concentrations above 3.0×10^{-2} M. Good extraction was obtained with 18-crown-6, but extraction with 15-crown-5, B-15-crown-5, DB-18-crown-6, and DC-18-crown-6 was incomplete. Better extraction was obtained at picric acid concentrations above 7.0×10^{-3} M. Quantitative stripping could be obtained with 4-5 M HCl, 2-5 M HNO_3, 5.0 M H_2SO_4, and 2.5-5 M $HClO_4$. Higher concentrations of cesium could be extracted provided the crown ether concentration is proportionally increased. Using the selective extraction capabilities of several crown ethers, cesium was separated from alkali and alkaline earth elements, zirconium, hafnium, and thorium.

2.4.3 Extraction - Crown Ether

The effectiveness of crown ethers for separating cesium and strontium from nitric acid solutions was investigated (Yakshin et al. 1992). Nitric acid solution concentrations ranged between 0.6 M and

9.0 M, with the initial cesium and strontium concentration at 10 mg/L. Crown ethers used include dibenzo-21-crown-7 (DB21C7), its adduct with a phophmolybdic heteropolyacid (DB21C7•HPMo), and the crown ether dicyclohexyl-18-crown-6 isomer A (DCH18C6A). The crown ether concentration was 0.1 M in chloroform or nitrobenzene. The crown ethers DCH18C6A and DB21C7 extract essentially no cesium, while DB21C7•HPMo extracts cesium over a HNO_3 range of 0.6 M to 3.0 M. At 3.0 M HNO_3 the D_{Cs} is 134 with 99% extraction in a single stage. Compared to strontium, only DCH18C6A showed significant extraction with over 98% in a single stage. At higher HNO_3 concentrations there is a decrease in D_{Cs}.

2.4.4 Extraction - Lowinox 22M46

The extraction of cesium from intermediate level liquid radioactive waste (NPP V1) was investigated using 2,2'-Methylene-bis (4-methyl-6-ter-butylphenol) (Lowinox 22M46) in nitrobenzene at high pH (Gulis and Mikulaj 1991). D_{Cs} of 4.4 was obtained for 0.5 M Lowinox 22M46 in nitrobenzene at pH 12.81 for a 5 minute extraction time. The use of other organic diluents resulted in a significant decrease in extraction efficiencies. Increasing the Lowinox 22M46 concentration increases D; however, at higher concentrations the aqueous and organic phases become nearly inseparable. A slight increase in D_{Cs} was observed in the presence of lithium, sodium, and potassium ions.

2.4.5 Ion Exchange - Copper Hexacyanferrate Resins

The removal of cesium from liquid effluent was investigated by passing the stream through a column of copper hexacyanferrate (CuCF) loaded resins (Singh and Ramaswamy 1991). The CuCF was loaded onto Indion-810 and Tulsion-A27MP basic anion exchange resins. Their efficiency for cesium removal was tested under both static and dynamic conditions. For feed solutions with ^{134}Cs (activity 10^{-3} $\mu Ci/ml$) Ds of 6×10^3 and 5.8×10^2 were obtained for the Indion and Tulsion resins, respectively. In column tests, using 3 g of the resin at flow rates 10-30 bed volumes/hour, very little breakthrough occurred, even after 1000 column volumes had been passed. In general, Tulsion based resins showed more tolerance towards acid and salts in the feed than the Indion based resins. However, the CUCF based exchangers are not suitable to treat acidic wastes, as oxidation to hexacyanoferrate Am(III) occurs for nitric acid concentrations >0.1 M. The presence of sodium and potassium in the waste stream had the effect of decreasing D_{Cs}, and the best results were obtained at pH 7-10.

2.4.6 Precipitation - Potassium-Cobalt Hexacyanoferrates

Several transition-metal hexacyanoferrate compounds have been tested for removal of ^{137}Cs from simulated liquid low level radioactive waste (LLLW) and contaminated process waste water (Kent et al. 1993). In this process several potassium-cobalt hexacyanoferrate (KCFC) ion exchange particles were prepared and obtained from different sources. The ion exchange particles were mixed with the solutions and allowed to settle. Decontamination factors as high as 35 were obtained for cesium (initial concentration 5.94×10^6 $\mu Ci/m^3$) from the simulated waste and DFs of 12 for the process wastewater. Each KCFC sample behaved in a different manner indicating that the method of preparation significantly influenced the cesium exchange properties. Cesium removal was influenced more by pH 10.7-13 than the solution compositions (i.e., cations present and concentrations). In addition, residual cyanide compounds were detected in the effluent stream and would require additional treatment before discharge to the environment.

2.4.7 Precipitation - PTA or NaTPB

The separation of cesium from the aqueous raffinate of reprocessed materials testing reactor (MTR) fuels has been investigated (Grossi et al. 1992). In one process cesium is directly precipitated with phosphotungstic acid (PTA) from the acidic waste. In the second process the waste first undergoes alkalinization followed by cesium precipitation with sodium tetraphenylborate (NaTPB). The acidic based process offers the advantage that less secondary waste will be generated, as no pH adjustment is required; however, the alkaline precipitation process is well known, and neutralization of the waste would be required before storage, anyway. Short descriptions of the cesium removal processes are described below.

Precipitation of cesium (initial concentration 20 mg/L) using PTA from a 1.1 M HNO_3 simulated material test reactor waste solution was evaluated. Between 2 M and 5 M in acid concentration the precipitation of Cs_2HPTA is promoted. Above 5 M acid the CsH_2PTA and Cs_2HPTA reactions are promoted. More than 12 hours of contact time are required to achieve DF_{Cs} near 100. It was suggested that to achieve higher DFs, additional contacting steps would be required, and the addition of KNO_3 to the feed should improve the recovery.

The second process involves alkalinization of the acidic waste with NaOH to $pH > 13$. Strontium and the actinides were co-precipitated in the alkaline waste leaving cesium. Using NaTPB (>200 mg/l) approximately 99% of the cesium was precipitated after a 30 minute reaction time.

2.4.8 Precipitation - Zinc Hexacyanocobaltate(III)

Zinc hexacyanocobaltate(III) was used to separate cesium from aqueous and simulated medium active waste (MAW) solutions by precipitation (Mekhail and Benyamin 1991). The uptake of cesium is >94% in the pH range from 0 to 6. D_{Cs} of approximately 7600 was obtained for simulated MAW with an initial cesium concentration of 10^{-3} M. Under similar conditions D_{Cs} of 3500 and 8900 were observed for zinc hexacyanoferrate(II) and zinc hexacyanoferrate(III), respectively. These Ds are an order of magnitude lower than that obtained in an aqueous solution, which suggests that species present in MAW had a significant influence on the separation.

2.4.9 Recirculating Liquid Membranes - D2EHPA

Cesium removal from liquid effluents was investigated using recirculating liquid membranes (RLM) (Blake and Ritchie 1992). Three liquid streams, feed, extractant, and strip are circulated through two membrane modules. The feed solution contacts the extractant stream at the membrane surface in the first module. This extractant stream is passed to a second membrane module where the strip solution is contacted. The extractant used was di-2-ethylhexylphosphate (D2EHPA) 20% by volume in kerosene. For a 1000 mg/L cesium feed at pH 7, $D > 10$; and D_{Sr} is on the order of 56,000. In solutions containing both cesium and strontium the transfer rate for cesium was 55% of the single-ion rate. The RLM process is not currently viable on a large scale compared to alternative processes and should be limited to small volumes with only one dominant cation (Blake and Ritchie 1992).

2.5 Iodine Separations

The ^{129}I is one of the contributors to long term risk as it has high solubility and mobility in groundwater. The long term risk for ^{129}I is a concern even below Class A LLW limits. In addition, the volatility of iodine precludes disposal in a borosilicate glass form. A special waste form may be required for iodine disposal. The separation of iodine from aqueous systems was studied using ion chromatography, extraction, isotope exchange, and combination air sparging and heat treatment processes.

2.5.1 Adsorption/Ion Chromatography

Preliminary concentration and separation of iodine is performed using a column filled with a platinum-coated copper (PCC) bed that converts all forms of iodine to iodide and selectively adsorbs the iodide (Lamb et al. 1992). The separation is completed by an anion chromatographic system. Several simulated fuel reprocessing solutions were prepared and spiked with ^{127}I. After adsorption on the PCC the iodide is stripped by 0.2 M NaOH. This strip solution is passed through the chromatographic separator column and the iodide eluted with 0.25 M HNO_3 in 5% methanol. Greater than 97% recovery was achieved for each of the simulated nuclear fuel reprocessing solutions with sample sizes ranging from μl to 500 ml quantities. A major concern is the destruction of the PCC bed in acid solutions with high nitrate concentrations. The authors negated this problem by reducing the nitrate ion concentration with the addition of metallic zinc.

2.5.2 Extraction and Isotope Exchange - TBP and NaI Carrier

Extraction and isotope exchange was investigated for the separation and preconcentration of ^{131}I and $^{131}IO_3$ from an aqueous system using TBP in toluene (Palagyi 1991). For the extraction experiments 1 M TBP in toluene was used and for the isotope exchange experiments 0.1 M I_2 in 1 M TBP in toluene was utilized. Greater than 95.5% separation efficiency was achieved for the extraction of ^{131}I from an aqueous feed for pH <5.5. At NaI carrier concentrations $<10^{-3}$ M greater than 96% separation efficiency was achieved for iodine. For iodate separations, the iodate removal was very slow unless catalyzed by iodide ions in an acid medium. Separation efficiencies $>97\%$ were obtained for $^{131}IO_3$ at >1 M HCl concentrations with 0.1 M I_2 in 1 M TBP in toluene. Other acids such as HNO_3 and H_2SO_4 showed similar trends as observed for HCl solutions. Based on the results, I, I_2, and IO_3 can be separated by isotope exchange from water at pH <0, while at pH 2 to 4 only I and I_2 can be separated. The I and I_2 can be separated from each other by extraction with TBP in toluene at pH 1-3. In mixtures of important fission products (i.e., strontium-yttrium, strontium-niobium, ruthenium-rhodium, cesium-barium, barium-lanthanum and cerium-praseodymium) only zirconium and rhodium were found to interfere with the isotopic exchange. This interference was suppressed by the addition of their carriers (e.g., 5 g/L as nitrates).

2.5.3 Heat Treatment and Air Sparging

Removal of residual iodine from nuclear fuel solutions was conducted using heat treatment and air sparging (Boukis and Henrich 1991). The process involved adding 10^{-4} M carrier iodine as KIO_3 followed by heat treatment for approximately 15 hours at 105°C. Subsequent sparging with air resulted in more than 99.9% of the I-129 removed from the fuel solution. A DF of 21 was achieved for the process. Variation of the carrier concentration between 10^{-3} and 10^{-5} did not significantly influence the removal, while much better removal was obtained at temperatures above 100°C. Nitrous acid and nitrous oxides must be removed from the solution to prevent reducing the iodate carrier to volatile I_2.

2.6 Nickel Separations

Variability of compositions within the Hanford tank wastes may necessitate the removal of ^{63}Ni to ensure that the LLW form does not exceed the class A limit. Recent research efforts involving nickel separations are primarily directed at the clean-up of industrial waste water streams. Nickel separations described below include precipitation, flotation, and extraction processes.

2.6.1 Extraction - Aliphatic Oxime

The extraction of nickel from a simulated manganese circuit raffinate was investigated using aliphatic oximes, in particular decanol oxime (DOX) (Redden and Groves 1993). DOX was diluted with an aromatic naphtha to 1 M and contacted in a stirred reactor with a feed containing nickel (12 g/L), chromium (84 g/L), and chloride (200 g/L) at a H^+ concentration of 0.4 M. The initial loading rate was relatively fast with 90% of the equilibrium nickel loading occurring in the first 5 minutes; however, over 60 minutes was required to reach the equilibrium loading of 12.4 g/L. Stripping was conducted using a 7.5 g/L HCl solution. Approximately 50% of the equilibrium loading was achieved in 5 minutes, but 240 minutes was required to reach the equilibrium nickel loading of 0.6 g/L. The decyl oxime degraded 12% per loading and stripping cycle, but was effectively regenerated by contacting the solvent phase with a neutralized hydroxylamine-hydrochloride solution. The stability of DOX was improved by adding decyl aldehyde to the solvent, which eliminated the regeneration stage.

2.6.2 Flotation - Dissolved-Air

Metal ions were separated from dilute aqueous solution by dissolved-air flotation (Lazaridis et al. 1992). Ion flotation using xanthates such as potassium oethyl-dithiocarbonate (KEX) was investigated. Removal of over 90% of the nickel (50 mg/L) was obtained at pH >4. At pH 8 nearly 100% removal of nickel was observed. In a copper-nickel mixture, copper was selectively removed through ion flotation, while the nickel remained in solution. In a iron-nickel mixture the nickel could be floated only at pH >7 where its hydroxide precipitate forms. Increasing the KEX concentration resulted in an increase of the nickel recovery.

2.6.3 Flotation - Adsorbing Colloid

The removal of Ni(II) from chromium stream electroplating wastewater was investigated using adsorbing colloid flotation (Sanciolo et al. 1992). This process consists of stripping the contaminants by adsorption or coprecipitation onto colloidal material followed by column flotation. The colloid was prepared in situ by the hydrolysis of added Fe(III) metal ions. Flotation was achieved by adding a dual surfactant system that consisted of sodium dodecylsulfate (SDS) and dodecanoic acid (DA). At a concentration of 200 ppm SDS and 100 ppm DA and pH>7.5, more than 99% of the nickel was floated. The dual surfactant system exhibited a synergistic effect in relation to the nickel removal. Increasing the pH or surfactant concentration effectively increases the nickel removal.

2.6.4 Precipitation - Oxalate

Oxalate precipitation was used to recover nickel from metal finishing industry waste acids and hydroxide sludges (Brooks 1993). Oxalic acid was added at 1.5 times the stoichiometric requirement for the nickel present. Recoveries between 92.5% and 99.9% were achieved for various types of nickel wastes (i.e., electrochemical machining sludges, spent catalysts, plating wastes, waste mineral acids) and initial nickel concentrations (0.29% to 25.0% by wt.). However, the removal of other metals from the waste was required before the nickel could be removed. The whole process consisted of several extraction, precipitation and ion-exchange steps to remove the other contaminant metals. Using a combination of oxalate precipitation and ion exchange recoveries of 99.9% were obtained from all of the nickel wastes with the exception of plating wastes.

2.7 Strontium Separations

Strontium-90 is a major contributor to radioactivity in the SST waste and also a concern as a significant source of heat generation in the final waste forms. As a result of the high activity, ^{90}Sr should be separated from the waste to ensure that the LLW form meets class A limits, and it must be separated from the bulk of the sludge components to minimize the volume of HLW that must be vitrified. Recent strontium separations include several membrane processes as well as adsorption and extraction methods.

2.7.1 Adsorption - Polyantimonic Acid

Adsorption of strontium on polyantimonic acid (PAA) from a 1.1 M HNO_3 simulated material test reactor waste solution was investigated (Grossi et al. 1992). A D_{Sr} of 118 was obtained, though the PAA exchange rate was very low. The PAA exchange capacity was 2.7 mg/g, and breakthrough did not occur until 400 column bed volumes had been passed. However, the authors reported that the commercial PAA product had poor mechanical or chemical stability.

2.7.2 Extraction - Crown Ether

Macrocyclic polyethers (crown ethers) soluble in a water insoluble organic compound were used to remove strontium from aqueous nitric acid waste solutions (Horwitz and Dietz 1992). The preferred organic phase is 0.2 M Dt-BuCH18C6 in 1-octonal with the organic extractant and aqueous acid feed ratio at 1:3. Contact times are about 30 seconds, and stripping may be accomplished by contacting the extractant with water. Depending on extractant, diluent, and acid concentrations, D_{Sr} ranged from near 0 to 80 in the examples presented. In general, the recovery improves with increasing nitric acid concentration up to 6 M.

2.7.3 Ion Exchange - Phenolic Resin

The selective uptake of strontium from solutions containing various amounts of sodium was investigated using phenolic resins synthesized from catechol, gallic acid, and beta-resorcylic acid (Samanta et al. 1992). Distribution ratio for strontium were as high as 6580 for the catechol-resorcinol-formaldehyde polymer in 1 M $NaNO_3$ + 0.1 M NaOH solutions. The ion exchange capacity of the dry resin was 8.53 meq/g. For the gallic acid-resorcinol-formaldehyde polymer,

D_{Sr} = 4920 was obtained. Increasing the concentration of alkali (up to 0.5 M) resulted in the enhanced uptake of strontium. The rate of strontium uptake was initially fast, followed by a rapid decrease, with the equilibrium rate reached after 100 minutes. These polymers have reasonably high affinities for strontium in alkaline waste solutions, even in the presence of sodium salts. Gallic acid-formaldehyde resin was more effective in removing strontium at the higher sodium concentrations, with the catechol-based resin better at lower sodium (<0.05 M) concentrations.

2.7.4 Emulsion Liquid Membrane - Crown Ether

The separation of strontium and calcium was investigated using emulsion liquid membranes stabilized with polyamine tenside, using 18-crown-6 and picric acid as carriers (Mikulaj and Vasekova 1991). For the membrane phase, 1,1,2,2 tetrachloroethane and 1,2,4,-trichlorobenzene were used, and polyamine tenside ECA 4360 was used to stabilize the membrane. With ECA 4360 the emulsion was stabilized for over 3 hours compared to 20 minutes obtained with SPAN 80. The outer solution consisted of $SrCl_2$ (10^{-5} M), $CaCl_2$ (10^{-5} M), picric acid (5 x 10^{-3} M), and 18-crown-6 (5 x 10^{-4} M). The membrane phase contained ECA 4360 (4% by wt.) in trichlorobenzene, tetrachloroethane, or toluene with an inner solution of HCl (0.5 M). Best results with respect to strontium yield and strontium/calcium separation factor were obtained by the trichlorobenzene membrane with a $\alpha_{Sr\text{-}Ca}$ of 1500.

2.7.5 Supported Liquid Membrane - Crown Ether

The removal of strontium and cesium from actual reprocessing wastes was investigated using supported liquid membranes (SLMs) constituted with crown ethers (Dozol, Garcia, and Sastre 1991). Strontium was extracted from reprocessing waste with an SLM constituted with DC-18-Crown-6 (0.5 M) in decanol (0.7 M) diluted in hexylbenzene. Initially, a fast transfer of ^{90}Sr through the membrane was observed, then the rate decreased, and after 100 hours the strontium transport stopped. Approximately 80% of the strontium was extracted from the reprocessing waste. Good selectivity for strontium was observed, compared to the actinides. In addition, experiments for simultaneous removal of strontium and cesium from simulant waste with SLMs were conducted. The highest distribution ratios were obtained for a mixture of DC-18-Crown-6 (0.5 M) + tBuB-21-Crown-7 (0.5 M) + decanol (0.8 M) in hexylbenzene. D_{Sr} = 32 and D_{Cs} = 1.54 corresponds to 80% of the strontium extracted and 33% of the cesium removed.

2.8 Technetium Separations

Technetium-99 is a contributor to the long term risk as a result of high solubility and mobility in groundwater. Consequently, technetium removal is required to minimize the long term risk associated with the LLW form. Recent research efforts on technetium separations are described below.

2.8.1 Extraction - Crown Ether

Macrocyclic polyethers soluble in a water insoluble organic compound were used to remove technetium from aqueous nitric acid waste solutions (Horwitz and Dietz 1992). Several crown ethers and extractants were evaluated. The preferred crown ether was 0.2 M Dt-BuCH18C6 in 1-octonal with the organic extractant and aqueous acid feed ratio at 1:3. Contact times are about 30 seconds, and stripping may be accomplished by contacting the extractant with water. For HNO_3 concentrations between 0.01 M and 3 M, D_{Tc} ranged from 0.12 to 1.85, respectively. At concentrations >3 M HNO_3, D_{Tc} remained essentially constant. In general, D_{Tc} improved with an increase in nitric acid concentration up to 6 M.

2.8.2 Extraction - APDC/NaDDC Chelation

Technetium was removed from LLW by chelation with sodium diethyl dithiocaramate (NaDDC) in a 3 N HCl solution and selective extraction into chloroform (Chiu et al. 1991). Radioactive contaminants were removed by carrier hydroxide precipitation and chelating extraction at pH 4. Using the NaDDC/$CHCl_3$ system at various HCl concentrations, enables separation and concentration of technetium from low level radioactive wastes. An average recovery of 90% of ^{99m}Tc tracer was achieved for radioactive sludge, environmental soil samples, and nuclear installation effluent. The best extraction efficiencies (>98%) were obtained from the aqueous effluent. DFs $> 10^5$ were obtained for ^{60}Co, ^{110m}Ag, ^{54}Mn, and ^{65}Zn.

In more recent work, ammonium tetramethylene dithiocarbamate (APDC) was used as the chelating agent for technetium removal from LLW (Chiu et al. 1992). For HCl concentrations >0.01 M, 99% of the technetium activity can be extracted into the organic phase. Back extraction efficiencies were >98.7% for a strip solution of 1 M NaOH and 3.5% H_2O_2. Greater than 91% recovery of ^{99}Tc was obtained from water, sludge, concentrate, and mixed-bed resins wastes.

3.0 References

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