Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Solvent Extraction Recovery of Byproduct ^{137}Cs and ^{90}Sr from HNO_3 Solutions—A Technology Review and Assessment

W. W. Schulz[a]; L. A. Bray[b]
[a] Rockwell Hanford Operations, Richland, Washington [b] Pacific Northwest Laboratory, Richland, Washington

To cite this Article Schulz, W. W. and Bray, L. A.(1987) 'Solvent Extraction Recovery of Byproduct ^{137}Cs and ^{90}Sr from HNO_3 Solutions—A Technology Review and Assessment', Separation Science and Technology, 22: 2, 191 — 214
To link to this Article: DOI: 10.1080/01496398708068948
URL: http://dx.doi.org/10.1080/01496398708068948

SEPARATION SCIENCE AND TECHNOLOGY, 22(2&3), pp. 191-214, 1987

Solvent Extraction Recovery of Byproduct ^{137}Cs and ^{90}Sr from HNO_3 Solutions—A Technology Review and Assessment

W. W. SCHULZ

ROCKWELL HANFORD OPERATIONS
P. O. Box 800
RICHLAND, WASHINGTON 99352

L. A. BRAY

PACIFIC NORTHWEST LABORATORY
P. O. Box 999
RICHLAND, WASHINGTON 99352

ABSTRACT

A principal purpose of this paper is to call out what is perceived to be a timely need for increased research to develop improved and new solvent extraction technology for recovery of ^{137}Cs and ^{90}Sr from strong ($\geq$0.5$\underline{M}$ HNO_3) acid media, technology which can be quickly scaled up to routine plant-scale operation with highly radioactive waste solutions when needed.

The present and forseeable future (2020) U.S. inventory of ^{137}Cs and ^{90}Sr is listed; much of this inventory is expected to be available only in strongly acidic nuclear waste solutions. Comparison of available methods - precipitation and ion exchange as well as solvent extraction - for recovering ^{137}Cs and ^{90}Sr from alkaline and acid media demonstrates, as expected, that very limited technology is available for use with strongly acidic solutions. Solvent extraction procedures which employ either macrocyclic polyethers (crown ethers) or dicarbolide, $H^+\{[\pi\text{-}(3)\text{-}1,\ 2\text{-}B_9C_2H_{11}Cl_2]_2Co\}^-$, to extract ^{137}Cs and ^{90}Sr from $\geq$0.5$\underline{M}$ HNO_3 solutions have recently been proposed. But, in their present state of development, both the crown ether and dicarbolide extraction

processes have several drawbacks and/or unknowns. Thus, the present results should be considered as a springboard and a spur not only to further development and testing of these particular compounds, but also to continue the search for other extractants which offer even greater potential for plant-scale recovery of byproduct cesium and strontium from acidic wastes.

INTRODUCTION

Interest in the U.S. in recovery and purification of so-called "by-products"[a] from aqueous nuclear fuel reprocessing high-level waste (HLW) solutions has waxed hot and then waned several times over the last quarter of a century. For example, in the early 1960's megacuries of ^{90}Sr were recovered at the U.S. Atomic Energy Commission (AEC)[b] Hanford Site for use in navigational buoys and in several military applications as well. This early success in recovery and utilization of by-product ^{90}Sr prompted one prospective contractor to the AEC to propose (in 1965) construction and operation of a plant to recover (and market commercially) various radioisotopes including ^{90}Sr, ^{137}Cs, and ^{147}Pm from Hanford defense HLW. A short two years later, the harsh economic realities were all too apparent -- there was no demand and no market for nuclear by-products. The proposed recovery/purification plant was not built, and the contractor was replaced.

During the last two decades in the U.S., interest in and application of technology for removing ^{137}Cs and ^{90}Sr from HLW has been motivated almost exclusively by waste management needs (e.g., removal of heat energy, inexpensive near surface disposal, etc.) rather than by potential use of separated nuclear byproducts. At the Hanford Site megacuries of both ^{137}Cs and ^{90}Sr have been removed from HLW generated in the period 1944 to 1972. The recovered radiocesium and radiostrontium have been purified, converted to solid ^{137}CsCl and ^{90}SrF$_2$, respectively, and placed in double-walled canisters for storage in water basins.

In the last year or two, however, the pendulum of beneficial uses of by-products has been on the upswing. Currently there is active interest in the U.S. concerning use of ^{137}Cs gamma radiation for sterilization of medical supplies and various fruits and other foodstuffs as well as for the treatment of sewage sludge. (Recent action of the U.S. government in banning further use of ethylene

---

[a] Uranium, plutonium, and, in some cases, neptunium are the products recovered by such reprocessing while both radioactive (e.g., ^{137}Cs, ^{90}Sr, ^{99}Tc, etc.) and inert (e.g., Rh, Pd, etc.) fission products are by-products.

[b] A predecessor of the present U.S. Department of Energy (DOE).

dibromide as a fumigant for fruit products has been a major driving force in the renewed consideration of ^{137}Cs and its properties.) Indeed, so strong is the current interest in beneficial uses of ^{137}Cs that licensed private U.S. irradiation facilities have placed orders for the entire inventory of encapsulated ^{137}CsCl at the Hanford Site. Although not nearly as intense as those for ^{137}Cs, there are also strong signs of renewed interest in beneficial applications of ^{90}Sr.

The recent activity concerning ^{137}Cs and ^{90}Sr has motivated us to conduct this examination of the present state of technology for solvent extraction of radiocesium and radiostrontium from HLW solutions. For waste management purposes, various solvent extraction processes for removal of ^{137}Cs and/or ^{90}Sr from alkaline or weak acid solutions have been developed on a bench-scale and, in at least one case, applied on a plant-scale. Ion exchange and precipitation, and, to a much smaller extent, solvent extraction processes for isolation of ^{137}Cs and ^{90}Sr from strong acid (HNO_3) waste solutions have also been developed. The major emphasis and thrust of this paper is to alert the separations chemistry community to what is perceived to be a timely need for research to develop improved and new solvent extraction technology for acid-side recovery of ^{137}Cs and ^{90}Sr, technology which can be quickly scaled up to large scale use if and when needed.

INVENTORY AND APPLICATIONS OF ^{137}Cs AND ^{90}Sr

Estimated Inventory

Table 1 summarizes amounts of ^{137}Cs and ^{90}Sr available in the U.S. from both defense and commercial sources. As indicated in Table 1, a substantial portion of the existing inventory of ^{137}Cs and ^{90}Sr at the Hanford Site has been recovered, purified, converted to either CsCl or SrF_2, and encapsulated as ^{137}CsCl and $^{90}SrF_2$, respectively. According to the present Hanford Waste Management Plan (3), ^{137}Cs will be removed from future (post 1983) waste but will not be purified and encapsulated.

There are no facilities at the U.S. DOE Savannah River Plant to purify or encapsulate either ^{137}Cs or ^{90}Sr. Although there currently are no plans to recover any Savannah River Plant by-product cesium and strontium, a recent DOE study examined the feasibility and projected costs of separation and encapsulation of ^{137}Cs and ^{90}Sr at Savannah River and those of recovery at Savannah River and shipping to Hanford as a dried solid sorbed on an ion exchange resin (1). Both approaches appear to be feasible if regulations permit shipment and the demand justifies costs for recovery and encapsulation of ^{137}Cs and ^{90}Sr.

Not unexpectedly, of course, current and, especially, future inventories of ^{137}Cs and ^{90}Sr in irradiated U.S. commercial reactor fuel far exceed - by about a factor of 10 - those available from U.S. defense sources. Stored spent commercial power reactor fuel represents the prime source of both ^{137}Cs and ^{90}Sr.

TABLE 1
Estimated U.S. Supply of ^{137}Cs and ^{90}Sr[a]

Source	Estimated Inventory, MCi ^{137}Cs	Estimated Inventory, MCi ^{90}Sr
DEFENSE WASTES		
Hanford Site		
Encapsulated[b]	70	40
Future (to 1995)[c]	50	42
Savannah River Plant		
Present[d]	100	120
Future (to 2000)[e]	1000	920
COMMERCIAL FUEL		
Present[f]	500	370
Future (to 2020)[g]	11,000	9,000

---

[a] Taken from data in References 1 and 2
[b] As ^{137}CsCl and ^{90}SrF$_2$, respectively
[c] From operation (1983 through 1995) of Hanford PUREX plant
[d] In existing tank waste
[e] From operation (1985 through 2000) of Savannah River PUREX processes
[f] Stored in water basins
[g] In spent fuel accumulated by 2020

Beneficial Uses

Tables 2 and 3, respectively, list some typical and important beneficial uses of ^{137}Cs and ^{90}Sr. Iotech, Inc. in Denver, Colorado is currently using Hanford-type ^{137}CsCl capsules for industrial-scale sterilization of medical supplies. A very active research program to demonstrate applicability of ^{137}Cs gamma radiation for disinfestation and preservation of various agricultural products (e.g., cherries, apples, hides, etc.) is currently in progress at the Pacific Northwest Laboratory in Richland, Washington (4). An industrial-scale irradiator [Cesium-137 Agricultural Commodities Irradiator (CACI)] for treating foodstuffs is being designed and built (5).

Applications of ^{90}Sr stem from its ability to function very effectively as a fuel for thermoelectric and thermomechanical power

TABLE 2
Some Beneficial Uses of ^{137}Cs

- FOOD PRESERVATION BY IRRADIATION
  - Dried Fruits and Nuts
  - Citrus Fruits
  - Fresh Pork
  - Shellfish
  - Spices
- STERILIZATION OF MEDICAL SUPPLIES
- IRRADIATION OF HIDES
- IRRADIATION OF MUNICIPAL SEWAGE SLUDGE

TABLE 3
Some Beneficial Uses of ^{90}Sr

- RADIOISOTOPE-FUELED THERMOELECTRIC GENERATORS (RTGs)
  - Remote Weather Stations
  - Remote Surveillance Stations
  - Navigational Aids
- RADIOISOTOPE-FUELED THERMOMECHANICAL GENERATORS (RTMGs)
  - Remote Emergency Power
- HEAT-SOURCE APPLICATIONS
  - Military Applications
  - Petroleum Applications

generators (e.g., Rankine, Brayton, and Stirling cycle engines). As indicated in Table 4, ^{90}Sr-powered RTG's (1 to 100 watts) have been used as a source of electric power for remote weather and surveillance stations and for various types of command and control systems. Vogt (6) has described progress toward construction of a 500 watt(e) RTG fueled with encapsulated $^{90}SrF_2$ from the Hanford Site. In addition to its use in RTGs and RTMGs, ^{90}Sr, when suitably encapsulated and shielded, can also be used as a valuable heat source.

RECOVERY PROCESSES

Alkaline and Acidic Feedstocks

High-level wastes (HLW) generated at the U.S. Hanford and Savannah River Sites are currently made alkaline by addition of NaOH and stored in underground tanks (Fig. 1). Iron(III) and various other transition group metal ions in the acidic HLW precipitate as hydrous oxides when NaOH is added to the acidic waste. These precipitates have a great affinity for ^{90}Sr and, thus, eventually all the ^{90}Sr in the waste reports to the solid ("sludge") phase. Conversely, ^{137}Cs does not precipitate and remains almost entirely in the alkaline (pH >9) liquid supernatant. Thus, from neutralized HLW, the sludge and alkaline supernatant phases constitute feed stocks for recovery of ^{90}Sr and ^{137}Cs, respectively.

There are, of course, no currently active plans in the U.S. to reprocess irradiated commercial power reactor fuel to recover uranium and plutonium values. But, when and if such reprocessing does occur, the HLW would almost certainly, following the practice in other countries, (e.g., France, United Kingdom, etc.), be stored as an acidic solution and eventually vitrified without ever being neutralized. Recovery of ^{137}Cs and/or ^{90}Sr from commercial power reactor fuel will thus have to deal with strongly acidic rather than alkaline media. A similar situation may eventually prevail even at the Hanford and Savannah River sites. At both locations, facilities to vitrify HLW are either being built or are planned; after existing backlogs of HLW are vitrified, it may be possible and/or desirable to eliminate further underground storage of neutralized HLW.

Removal/Recovery of ^{137}Cs from Alkaline Media

Listed in Table 5 are various precipitation, ion exchange, and solvent extraction processes which have been developed and, in some cases, used in large-scale removal and/or recovery of ^{137}Cs from alkaline waste solutions. Some amplifying comments on use of these procedures are provided in the following text.

Precipitation Processes. In the 1950's, investigators at the Hanford Site examined many different metal ferrocyanide and ferricyanide compounds to co-precipitate (or scavenge) ^{137}Cs from aged,

TABLE 4
Terrestrial Applications of ^{90}Sr-Fueled RTGs[a]

Generator Model	No. Mfd	Power, Watts	Year	Application	Status
Sentry	1	10	1961	Arctic weather station	2 years service
SNAP-7 Series	6	10-60	1961-65	USCG - USN	In storage
Sentinel 25	24	25	1966-67	Subsea communication	20 operating or being refurbished
Sentinel 3	3	3	1967	Subsea	In storage
Sentinel 8	23	8	1968-82	Weather communication	Operating
Sentinel 100F	1	100	1972	Computer power source	Scheduled for operation
Sentinel 15	4	1	1982	Communications relay	Operating

[a] Taken from Reference 2.

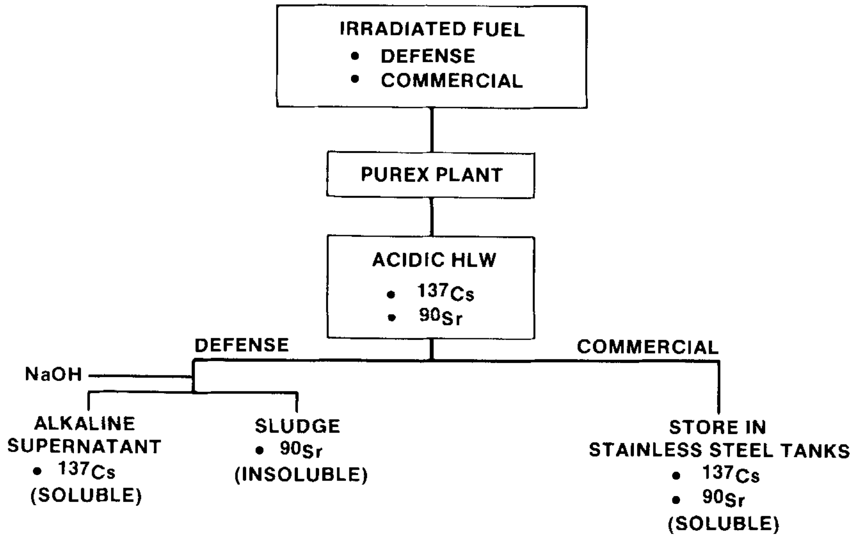

Fig. 1. ^{137}Cs and ^{90}Sr in Defense and Commercial High Level Waste

alkaline nitrate waste solutions. Highly successful results were obtained by precipitation of $Cs_2Ni[Fe(CN)_6]$; and, in the middle 1950's large-scale removal of ^{137}Cs from aged $BiPO_4$ process alkaline wastes was performed by precipitation of this compound. Later workers adapted the nickel ferrocyanide precipitation process to efficient removal and recovery of ^{137}Cs from freshly-produced Hanford PUREX plant high-level waste.

More recently (1982), Lee, Kilpatrick and others at the Savannah River Site studied application of the well-known analytical reagent, tetraphenylboron, to removal of ^{137}Cs from the large volume of alkaline wastes stored at that site. A successful test of the proposed precipitation scheme with actual waste was performed in 1984. Eventual routine plant-scale operation of the tetraphenylboron precipitation process is anticipated.

Ion Exchange Processes. Fixed beds of cation exchangers have long been used at the Hanford Site to recover and purify megacurie amounts of ^{137}Cs from alkaline waste solutions. Both inorganic (e.g., synthetic zeolites) and special organic (e.g., Duolite ARC-359) cation exchange materials have been used in plant-scale operations. The Duolite ARC-359 resin is particularly useful for feeds which contain sufficient NaOH to attack and dissolve aluminosilicate materials. Concentrated $(NH_4)_2CO_3$ solutions elute sorbed cesium efficiently; simple boiling of the eluate serves to reconsti-

TABLE 5
Methods for Removal/Recovery of ^{137}Cs from Alkaline Wastes

Method	Reagent	References
Precipitation		
	● Metal ferrocyanides and ferricyanides	7-15
	● Tetraphenylboron[a]	16
Ion Exchange		
	● DECALSO[b]	10, 17-20
	● LINDE AW-500[c]	21-24
	● IONSIV IE-95[c]	25
	● ZEOLON 900[d]	26-29
	● ARC-359[e]	25, 30-34
Solvent Extraction		
	● BAMBP[f]	35-37
	● Dipicrylamine - nitrobenzene	38-42
	● Tetraphenylboron - methylisobutylketone	43, 44
	● Polybromides - nitrobenzene	45, 46
	● Polyiodides - nitrobenzene	47
	● 2-Thenoyltrifluoroacetone	48

---

[a] Available from AAF Inc., Marietta, GA, for example.

[b] An aluminosilicate gel made by Ionic Chemical Co., Pfaudler Permutit, Inc., Birmingham, NJ.

[c] A synthetic zeolite made by Union Carbide Corporation, Tarrytown, NY.

[d] A synthetic zeolite made by Norton Co., Akron, OH.

[e] An organic elution exchanger made by Diamond Shamrock Corp., Redwood City, CA.

[f] 4-sec-butyl-2(α-methylbenzyl)phenol.

tute the eluent. IONSIV IE-96 has recently been chosen for use in removing ^{137}Cs from alkaline waste solutions stored at the former West Valley, New York fuel reprocessing site.

Solvent Extraction Processes. Various solvent extraction processes for removal and/or recovery of ^{137}Cs from alkaline media have been demonstrated on a bench- and, in some cases, on a pilot-plant scale. For example, Horner at the Oak Ridge National Laboratory in the early 1960's found that phenols such as 4-sec-butyl-2-(α-methylbenzyl)phenol (BAMBP) extract cesium well from aqueous phases at pH's above 10. Subsequently, Bray and Richardson at the Hanford site developed a BAMBP extraction process for removal of ^{137}Cs from various Hanford site wastes.

Kyrš and his colleagues in Czechoslovakia reported in the period 1960 to 1962 that nitrobenzene solutions of dipicrylamine will selectively extract ^{137}Cs from alkaline aqueous solutions. Bray and Richardson developed a dipicrylamine solvent extraction process for removal of ^{137}Cs from various Hanford alkaline wastes; this process was demonstrated on a pilot-plant scale with synthetic waste solutions. The toxicity of nitrobenzene is a recognized disadvantage of the dipicrylamine extraction process.

Other systems and/or extractants studied for extraction of ^{137}Cs from alkaline wastes include: tetraphenylboron-methylisobutylketone; polybromides-nitrobenzene; polyiodides-nitrobenzene; and 2-thenoyltrifluoroacetone.

Removal/Recovery of ^{137}Cs from Acidic Media

Listed in Table 6 are various precipitation, ion exchange, and solvent extraction processes which have been developed and, in one case, used in large-scale removal and/or recovery of ^{137}Cs from acidic waste solutions. The following text provides some explanatory information about these procedures.

Precipitation Processes. In strong (0.5 to 2.0M) HNO_3 solutions cesium ion reacts with phosphotungstate ion to produce an insoluble precipitate. This chemistry forms the basis of a precipitation process which has been used on a large-scale at the Hanford Site to recover >95% of the ^{137}Cs from PUREX process HLW. The cesium phosphotungstate precipitate is soluble in NaOH solutions; ion exchange procedures can be used to concentrate and purify ^{137}Cs from the resulting NaOH solution.

Ion Exchange Processes. Ion exchange processes for recovery of ^{137}Cs from acid waste solutions have been developed. These processes employ inorganic ion exchangers such as titanium phosphate, zirconium phosphate, and ferrocyanide molybdate. The materials are expensive and not readily available; for these reasons, processes which employ them have not been used for plant-scale recovery of ^{137}Cs from acidic medium.

TABLE 6
Methods for Removal/Recovery of ^{137}Cs from Acidic Wastes

Method	Reagent	References
Precipitation		
	● Phosphotungstic Acid ($0.5-2.0\underline{M}$ HNO_3)	49-52
Ion Exchange		
	● Titanium phosphate	53, 54
	● Zirconium phosphate	55, 56
	● Ferrocyanide molybdate	57
Solvent Extraction		
	● BAMBP-HDEHP-diluent[a] (pH 4)	58-61
	● PP-HDEHP-diluent[b] (pH 4-6)	62
	● Crown ether-HDEHP-(or HDDNS[c])-diluent	63-66
	● $H^+CoB_2^-$-Nitrobenzene-CCl_4[d] ($0.5\underline{M}$ HNO_3)	67-76
	● TBP-NNS-Crown XVII-diluent[e] ($3\underline{M}$ HNO_3)	77

---

[a] HDEHP = bis(2-ethylhexyl)phosphoric acid

[b] PP = 2-phenylphenol

[c] HDDNS = didodecylnapthalene sulfonic acid

[d] $H^+CoB_2^-$ = Dicarbolide,
$H^+\{[\pi-(3)-1,2-B_9C_2H_{11}Cl_2]_2Co\}^-$

[e] NNS = dinonylnapthalene sulfonic acid
Crown XVII = bis 4,4'-(5)[1-hydroxy-2-ethylhexyl]benzo 18-crown-6

Solvent Extraction Processes. Bray and Keder at the Battelle Pacific Northwest Laboratory found that mixtures of BAMBP and HDEHP synergistically extract both Cs^+ and Sr^{2+} from dilute (pH 4-6) acid waste solutions. An extraction process (CSREX process) based upon this synergistic effect for extraction and separation (by selective stripping) of Cs^+, Sr^{2+}, and trivalent lanthanides was successfully demonstrated on a pilot plant scale with simulated waste solution. Because of concern about the radiation and chemical stability of the BAMBP extractant, the CSREX process was not used on a plant scale.

Later (1974), Smelov and Lanin reported that a mixture of HDEHP and 2-phenylphenol would synergistically extract Cs^+ and Rb^+ from dilute acidic media.

McDowell and various coworkers have studied extraction of Cs^+ and other alkali metal ions from dilute acidic (pH 2 to 6) media by mixtures of various macrocyclic polyethers (crown ethers) and HDEHP or didodecylnapthalene sulfonic acid (HDDNS). The latter two organic cation exchangers provide a means of transferring the crown ether-Cs^+ complex into the organic phase; HDEHP and HDDNS also produce a synergistic extractant. No plant scale application of crown ether-HDEHP (or HDDNS) solvents for recovery of ^{137}Cs from dilute acid media has been made.

Davis and his coworkers at the University of South Carolina have scored what appears to be a real breakthrough in developing a practicable solvent extraction process for removal/recovery of ^{137}Cs from strong ($\geq$0.5M) HNO_3 solutions. Davis et al. report that certain 4-component organic solutions containing TBP (tri-n-butylphosphate), NNS (dinonylnapthalene sulfonic acid), a macrocyclic polyether (crown compound), and a hydrocarbon diluent selectively extract Cs^+ from simulated (3M HNO_3) PUREX process HLW.

Of several 4-component extractants studied by Davis et al., the most efficient cesium extractant was a solution of the composition 27 vol% TBP-5 vol% NNS-68 vol% kerosene-0.05M Crown XVII. (Crown XVII is bis 4,4',(5)[1-hydroxy-2-ethylhexyl]benzo-18-Crown-6., Fig. 2). For an equal volume contact of this particular organic solution with simulated PUREX HLW (3M HNO_3) containing 0.006M Cs at 23-25°C, the distribution ratio for Cs (D_{Cs}) is 1.6. Under these conditions, $D_{Zr} = 2.1$ while $D_{others} \leq 0.31$. The high D_{Zr} is attributed to the well-known propensity of TBP to extract zirconium from strong HNO_3 solutions.

In related tests, Davis et al. found that D_{Cs} decreased from 1.6 to 1.0 when the TBP-NNS-Crown XVII-kerosene solution was irradiated to an exposure of 10^7 rad. Dilute (0.5 to 1.0M) HNO_3 solutions can be used to strip Cs from the 4-component extractant; such stripping does not appear to be entirely effective, however. For example, data plotted in Fig. 3 of Reference 73 indicates six equal volume contacts of a pregnant TBP-NNS-Crown XVII-kerosene solution only removed about 80% of the cesium.

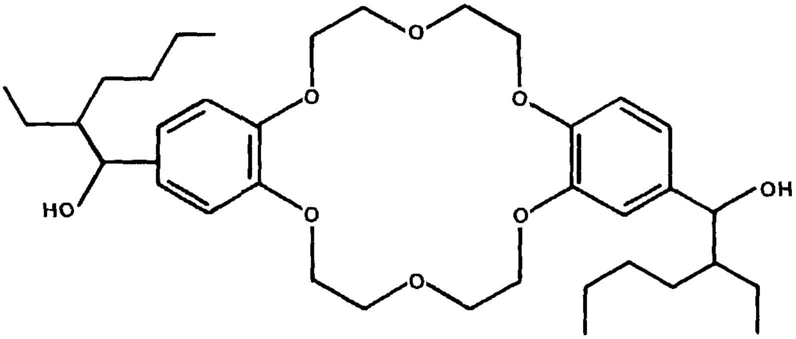

Fig. 2. CROWN XVII: bis 4,4'(5')[1-hydroxy-2-ethylhexyl]benzo 18-crown-6

For almost a decade now, Kyrš, Rais, and their associates at the Nuclear Research Institute in Czechoslovakia have pioneered use of the compound "dicarbolide", $H^+\{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}Cl_2]_2Co\}^-$ in solvent extraction of Cs^+ from HNO_3 solutions. Small concentrations of dicarbolide dissolved in a polar solvent such as nitrobenzene effectively and preferentially extract Cs from aqueous 0.5M HNO_3; under these conditions, ion pairs, e.g., Cs^+B^-($B^- = \{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}Cl_2]_2Co\}^-$) exist in the organic phase.

Kyrš et al. have established that Cs^+ can be readily stripped from the dicarbolide-nitrobenzene phase by strong (i.e., $\geq$3M HNO_3) solutions. The Czechoslovakian group has also conducted various experiments which suggest that cesium extraction properties of the dicarbolide extractant may not be seriously impaired by large doses of gamma irradiation. Results of bench-scale tests of extraction of ^{137}Cs from actual acidic high level waste solutions have been reported.

The extensive research of the Czech scientists on properties and application of the dicarbolide extractant is well documented. To our knowledge, however, scientists in other countries have not conducted similar studies.

Further discussion of the significance of the results of Davis, et al. and of Kyrš, Rais, et al. to development of a practicable process for plant-scale removal of ^{137}Cs from actual PUREX process HLW is given later (cf. pp. 19-20).

Removal/Recovery of ^{90}Sr from Acidic Media

All the processes developed for recovery of large amounts of ^{90}Sr are intended for use with acidic media. As noted in Fig. 1,

^{90}Sr coprecipitates with Fe(III) when U.S. defense wastes are made alkaline.

Table 7 lists the various precipitation, ion exchange and solvent extraction processes which have been developed for removal and recovery of ^{90}Sr from acidic media. The text accompanying Table 7 provides additional information about these processes.

Precipitation Processes. Lead sulfate carrier precipitation of ^{90}Sr from dilute HNO_3 solutions was developed at Hanford in 1961. After successful pilot-plant scale tests, the precipitation scheme was used to recover megacuries of ^{90}Sr from HLW. The lead sulfate carrier precipitation technology was also used to recover ^{90}Sr from dilute HNO_3 solutions of dissolved sludge (cf. Fig. 1).

Ion Exchange Processes. The inorganic ion exchanger, antimonic acid, has excellent affinity, and good specificity too, for sorbing ^{90}Sr from strong (0.5 to 7M HNO_3) acid waste solutions. European

TABLE 7
Methods for Removal/Recovery of ^{90}Sr from Acidic Wastes

Method	Reagent	References
Precipitation		
	• Lead Sulfate Carrier (pH 1-2)	78-81
Ion Exchange		
	• Antimonic Acid (0.5-7M HNO_3)	54-57, 82, 83
Solvent Extraction		
	• HDEHP-TBP-dodecane (pH = 4)	35, 37, 84-86
	• $H^+CoB_2^-$-Nitrobenzene-CCl_4[a] (0.5M HNO_3)[b]	67-76
	• TBP-NNS-Crown XVI-diluent[c] (3M HNO_3)	77

---

[a] $H^+CoB_2^-$ = dicarbolide (cf. Table 6)

[b] With addition of suitable complexing agent (e.g., polyethylene glycol, etc.) added to the aqueous phase.

[c] Crown XVI = bis 4,4'-(5)(1-hydroxyheptyl)cyclohexo-18-crown-6

investigators, in particular, have extensively studied and tested application of antimonic acid to recovery of ^{90}Sr from PUREX process HLW. Major disadvantages of antimonic acid include poor loading kinetics and the inefficiency of common mineral acid solutions in eluting sorbed ^{90}Sr. The former disadvantage can be partially overcome by operation at elevated temperature while Ag(I) and Pb(II) solutions will elute ^{90}Sr.

Solvent Extraction Processes. Bis-(2-ethylhexyl)phosphoric acid (HDEHP) diluted with TBP and a hydrocarbon diluent is a well-known and proven effective extractant for ^{90}Sr from dilute (pH 4-6) acid solutions. The HDEHP extraction process was first (1962-1963) investigated by Horner and Wischow at the Oak Ridge National Laboratory and then modified by Schulz and Richardson for plant-scale application. The HDEHP process was used for over 10 years in the Hanford B Plant to recover and purify about 40 megacuries of ^{90}Sr from acidified PUREX process sludge (cf. Fig. 1) hydraulically mined from underground tanks. In the process used at Hanford, various organic chelating agents (e.g., EDTA, citric acid, HEDTA, hydroxyacetic acid) were added to the acidic waste which was then adjusted to pH 5 by addition of NaOH. The HDEHP-TBP-dodecane solvent coextracted ^{90}Sr and fission product rare earths which were then separated by selective stripping agents.

Although the HDEHP ^{90}Sr extraction process performed very well, it did so at an unforeseen high price. The organic reagents used to complex iron, aluminum and other inert metals and prevent their extraction along with the ^{90}Sr are very resistant to either chemical or radiolytic degradation. High concentrations of such organic compounds in the aqueous raffinate from the ^{90}Sr extraction step prevent substantial evaporation of the raffinate. Moreover, these organic reagents also complexed ^{241}Am and the plutonium in the acid feed to the HDEHP extraction process. The net result was generation of about four million gallons of so-called Complex Concentrate currently stored in underground tanks. Future disposal of this waste will require treatment to make it a non-TRU waste and/or to destroy residual organic compounds.

Duplicating their experience with Cs, Davis et al. report that a 4-component organic extractant containing 27 vol% TBP, 5 vol% NNS-68 vol% kerosene-0.02M Crown XVI selectively extracts Sr^{2+} from simulated PUREX HLW (3M HNO_3). (Crown XVI is bis 4,4'-(5')(1-hydroxyheptyl) cyclohexo 18-crown-6; Fig. 3). For an equal volume contact of this latter 4-component solvent with simulated PUREX HLW (3.0M HNO_3) containing 0.003M Sr^{2+} at 23-25°C, D_{Sr} is 2.0. Under these conditions, D_{Zr} = 2.0, D_{Ba} = 2.4, and $D_{others} \leq 0.16$. D_{Sr} decreased from 2.0 to 1.6 when the TBP-NNS-Crown XVI kerosene solvent was irradiated to an exposure of 10^7 rad. Davis et al. state that, just as the case for Cs^+, dilute HNO_3 solutions strip Sr from the Crown XVI solvent; data plotted in Fig. 4 of Reference 73 do not entirely support this latter contention. Further discussion of the significance of the results of

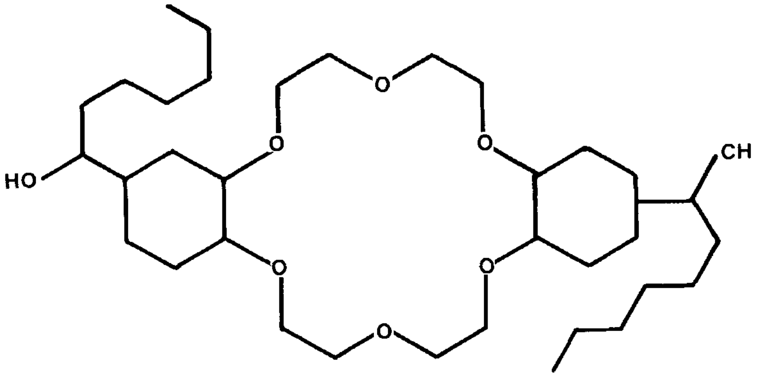

Fig. 3. CROWN XVI: bis 4,4'(5')[1-hydroxy-heptyl]cyclohexo 18-crown-6

Davis et al. to development of an engineering-scale process for removal/recovery of ^{90}Sr from actual PUREX HLW is presented later (*cf*. pp. 19-20).

Results obtained by Kyrš, Rais, and their Czechoslovakian colleagues indicate dicarbolide-nitro benzene will extract Sr^{2+} very efficiently from aqueous 0.5M HNO_3 provided a suitable complexing agent [e.g., a polyethyleneglycol (PEG), crown ether compound containing the grouping $-\underset{\overset{\|}{O}}{\overset{|}{P}}-CH_2-\underset{\overset{\|}{O}}{\overset{|}{P}}-$, etc.] is added to the aqueous phase. The Czech workers prefer to use an inexpensive and commercially-available PEG sold in Czechoslovakia under the tradename Slovafol 909.

Strong ($\geq$3M HNO_3) solutions strip Sr^{2+} from the dicarbolide-nitrobenzene extract. Use of the affinity of $H^+CoB_2^-$-nitrobenzene solutions for Sr^{2+} has been made in devising analytical procedures for ^{90}Sr in biological media. But, tests of dicarbolide extraction of ^{90}Sr from PUREX process HLW have apparently not been made.

ACID-SIDE SOLVENT EXTRACTION OF ^{137}Cs AND/OR ^{90}Sr

Some Theoretical Considerations

Clearly, a complete discussion of all the reasons why conventional liquid-liquid extraction reagents (e.g., organophosphates, amines, etc.) do not extract Cs^+ and Sr^{2+} from strong HNO_3 media while carbolide and some crown ethers do is outside the scope of this paper. But, a statement of some of the important reasons underlying these observed phenomena is worthwhile.

Because of their relatively large ionic radii (volume) and low charge, Cs^+ and Sr^{2+} have a low charge density. As a consequence, the energy of the bond between large mono- and divalent cations and functional groups (e.g., P=O) of organic extractants is not sufficient to dehydrate (i.e., remove water molecules) such large cations. The net result is that most commonly used reagents do not extract either Cs^+ or Sr^{2+} from aqueous solutions.

To compensate for charge density effects special organic extractants for alkali and alkaline earth ions from aqueous media must be found. One class of such extractants is the macrocyclic polyethers (crown ethers). Because of their cyclical nature, some of the crown ethers possess cage structures which are of exactly the correct dimensions to accommodate Cs^+, Sr^{2+} and other alkali and alkaline earth metal ions. Energetics for crown ether extraction of these ions from aqueous solutions are favorable since little or no change in conformational energy of the extractant molecule is involved. One difficulty with crown ether extractants, as noted previously in this paper, is that the extracted Cs^+ or Sr^{2+} is held so tightly it is difficult to find a suitable stripping agent.

An alternative approach to extracting alkali and alkaline earth metal ions from aqueous solutions consists of using an acidic reagent which, when dissolved in a polar solvent, is capable of forming an organic-phase soluble "ion association" type of complex with the metal ion. This approach has been extensively investigated by Czechoslovakian scientists (cf. Tables 5-7). Typical acidic reagents used include polyiodides, polybromides, dipicrylamine, and, more recently, dicarbolide.

Practical Considerations

The crown ether processes of Davis et al. and the dicarbolide processes of Kyrš, Rais, et al. are both potentially the sought for practicable solvent extraction schemes for routine engineering-scale recovery of ^{137}Cs and ^{90}Sr from strong HNO$_3$ solutions. But, to realize this potential, many uncertainties and gaps in the existing data bases must be resolved. Important issues include:

- Commercial availability of exotic reagent
- Inadequate stripping agent/performance (crown ether)
- Toxic diluent required (dicarbolide)
- Potential radiolytic generation of corrosive chloride ion (dicarbolide)
- Insufficient or nonexistent tests with actual PUREX process HLW
- Decontamination performance
- No countercurrent test data
- Application to coextraction of ^{137}Cs and ^{90}Sr
- Reference chemical process flowsheet
- Process economics

Only small amounts of the crown ethers (XVI and XVII, Figs. 2 and 3) recommended by Davis et al. for extraction of ^{90}Sr and ^{137}Cs, respectively, have apparently ever been synthesized. Kyrs and Rais state that 300 kg of dicarbolide have recently been prepared by a Czechoslovakian chemical firm. Reliable synthetic procedures and sources of large amounts of adequately pure crown ethers and dicarbolide are obviously needed before plant-scale use of these extractants can be seriously considered.

Limited tests of the dicarbolide reagent with actual PUREX HLW have been performed. Crown ethers XVI and XVII have been tested only on a batch-scale with synthetic waste. Extensive tests of these reagents under countercurrent conditions with actual HLW are needed to confirm their ability to recover and decontaminate radiocesium and radiostrontium.

To function as an effective cesium extractant, the dicarbolide compound must be dissolved in a polar solvent; the toxicity of the preferred diluent, nitrobenzene, is a strong deterrent to plant scale applications. Another potential disadvantage to the dicarbolide reagent is that radiolytic attack might generate sufficient chloride ion to cause excessive corrosion of stainless steel equipment.

Obviously, much further bench-scale work is needed to resolve concern about the suitability of dicarbolide and crown ethers XVI and XVII for routine recovery of megacuries of ^{137}Cs and ^{90}Sr. Accompanying engineering studies to define practical chemical flowsheets and to establish process economics are also a necessity.

SUMMARY AND CONCLUSIONS

The demand by U.S. industrial firms for separated and purified ^{137}Cs is at an all time high; demand for this radionuclide for various irradiating purposes in the U.S. is expected to continue to grow. Although currently nowhere near as high as that for ^{137}Cs, interest in potential applications of ^{90}Sr continues to be maintained. Two important factors which influence the future demand for ^{90}Sr are the availability and cost of a large supply of this byproduct.

The acidic HLW resulting from processing of U.S. defense production reactor fuels and, perhaps eventually, commercial power reactor fuels is a logical and attractive source of byproduct ^{137}Cs and ^{90}Sr. Proven continuous countercurrent solvent extraction processes suitable for engineering-scale recovery and purification of ^{137}Cs and ^{90}Sr, either separately or in combination, do not now exist; such processes need to be developed and demonstrated.

Recent results of Davis et al. (crown ethers) and of Rais, Kyrs et al. (dicarbolide) offer great promise that the desired plant-scale ^{137}Cs and ^{90}Sr solvent extraction processes can indeed be realized. But, in their present state of development, both the crown ether and dicarbolide extraction processes have several drawbacks and/or unknowns, e.g., exotic extractants not commercially available in large quantities, inefficient stripping reagents, nonexistent or insufficient countercurrent tests with actual waste solutions, potential corrosion problems, etc. Thus, the present results should be considered only as a springboard and a spur not only to further development and testing of dicarbolide and crown ether extractants but also to continue to search for other extractants which offer even greater potential for plant-scale recovery of byproduct cesium and strontium.

The task of finding practicable acid-side ^{137}Cs and ^{90}Sr solvent extraction processes is a challenging and difficult one which will require all the innovative skills of separation specialists. Success in this venture, however, will not only provide great intellectual and scientific satisfaction but will also have a significant and beneficial impact upon cost and availability of these two radionuclides.

REFERENCES

1. Jicha, J. J. Jr. and W. C. Remini, in *Waste Management '85*, R. G. Post and M. E. Wacks, Eds., Vol. 1, p. 529, 1985.

2. U.S. Department of Energy, "Department of Energy Plan for Recovery and Utilization of Nuclear Byproducts from Defense Wastes - Executive Summary", U.S. DOE Report DOE/DP-0013, Vol. 2, 1983.

3. U.S. Department of Energy, "Hanford Waste Management Plan", U.S. DOE Report, Richland, WA, 1984.

4. Eakin, D. E., G. L. Tingey, D. B. Anderson, and F. P. Hungate, in *Waste Management '85*, R. G. Post and M. E. Wacks, Eds., Vol. 1, p. 557, 1985.

5. Farrar, H. IV, G. Subbaraman, C. C. Conners, and J. P. Page, in *Waste Management '85*, R. G. Post and M. E. Wacks, Eds., Vol. 1, p. 551, 1985.

6. Vogt, J. F. in *Waste Management '85*, R. G. Post and M. E. Wacks, Eds., Vol. 1, p. 575, 1985.

7. Van Tuyl, H. H., U.S. AEC Report HW-48830, General Electric Co., Richland, WA, 1957.

8. Van Tuyl, H. H. and R. L. Moore, *Ind. Eng. Chem.*, *51*, 741, 1959.

9. Van Tuyl, H. H., *U.S. Patent* 2,985,505, 1961.

10. Bray, L. A. and H. H. Van Tuyl, U.S. AEC Report HW-70874, General Electric Co., Richland, WA, 1961.

11. Burns, R. E., W. E. Clifford, and R. L. Brandt, U.S. AEC Report 31444, General Electric Co., Richland, WA, 1954.

12. Stedwell, M. J. and R. E. Burns, *Chem. Engr. Progr.*, *53*, 93, 1957.

13. Barton, G. B., J. L. Hepworth, E. D. McClanahan, Jr., R. L. Moore, and H. H. Van Tuyl, *Ind. Eng. Chem.*, *50*, 212, 1958.

14. Hepworth, J. L., E. D. McClanahan, and R. L. Moore, U.S. AEC Report HW-48832, General Electric Co., Richland, WA, 1957.

15. Beard, S. J. and W. C. Schmidt, U.S. AEC Report HW-75051, General Electric Co., Richland, WA, 1962.

16. Lee, L. M. and L. L. Kilpatrick, U.S. DOE Report DP-1636, E. I. du Pont de Nemours & Co., Aiken, SC, 1982.

17. Bray, L. A., U.S. AEC Report BNWL-288, Battelle Pacific Northwest Laboratory, Richland, WA, 1967.

18. Ames, L. L., Jr., U.S. AEC Report HW-70768, General Electric Co., Richland, WA, 1961.

19. Ames, L. L., Jr. and J. L. Nelson, U.S. AEC Report HW-69263, General Electric Co., Richland, WA, 1961.

20. Lewis, R. E., T. A. Butler, and E. Lamb, U.S. AEC Report ORNL-3765, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

21. Mercer, B. W. and L. L. Ames, Jr., U.S. AEC Report HW-78461, General Electric Co., Richland, WA, 1963.

22. Nelson, J. L. and B. W. Mercer, U.S. AEC Report HW-76449, General Electric Co., Richland, WA, 1963.

23. Popovich, R. P., U.S. AEC Report HW-83461, General Electric Co., Richland, WA, 1964.

24. Brandt, H. L., U.S. AEC Report ARH-1639, Atlantic Richfield Hanford Co., Richland, WA, 1970.

25. Bray, L. A., L. K. Holton, T. R. Myers, G. M. Richardson, and B. M. Wise, U.S. DOE Report PNL-4969, Battelle Pacific Northwest Laboratory, Richland, WA, 1984.

26. Ames, L. L., Jr. and K. C. Knoll, U.S. AEC Report HW-74609, General Electric Co., Richland, WA, 1962.

27. Nelson, J. L., G. J. Alkire, and B. W. Mercer, *Ind. Eng. Chem. Process Design Develop*, *3*, 143, 1964.

28. Bray, L. A. and H. T. Fullam, in *Advances in Chemistry Series No. 101*, American Chemical Society, Washington, D.C., p. 450, 1971.

29. Buckingham, J. S., U.S. ERDA Report RHO-CD-739, Rockwell Hanford Operations, Richland, WA, 1979.

30. Baumgarten, P. K., M. A. Ebra, L. L. Kilpatrick, and L. M. Lee, U.S. DOE Report DP-MS-80-91, E. I. du Pont de Nemours & Co., Aiken, SC, 1980.

31. Wallace, R. M. and J. R. Wiley, U.S. AEC Report DP-1388, E. I. du Pont de Nemours & Co., Aiken SC, 1975.

32. Wallace, R. M. and R. B. Ferguson, U.S. AEC Report DP-MS-80-65 Rev., E. I. du Pont de Nemours & Co., Aiken, SC, 1980.

33. Wiley, J. R., U.S. AEC Report DP-1436, E. I. du Pont de Nemours & Co., Aiken, SC, 1976.

34. Wiley, J. R., U.S. AEC Report DP-1408, E. I. du Pont de Nemours & Co., Aiken, SC, 1976.

35. Horner, D. E., K. B. Brown, D. J. Crouse, and B. Weaver, *Nucl. Sci. Eng.*, *17*, 234, 1963.

36. Bray, L. A., U.S. AEC Report BNWL-68, Pacific Northwest Laboratory, Richland, WA, 1965.

37. Richardson, G. L., U.S. AEC Report HW-80686, General Electric Co., Richland, WA, 1964.

38. Bray, L. A. and F. P. Roberts, U.S. AEC Report HW-76222, General Electric Co., Richland, WA, 1963.

39. Richardson, G. L., U.S. AEC Report HW-75447, General Electric Co., Richland, WA, 1963.

40. Kyrš, M., J. Pelcik, and P. Polansky, *Colln. Czech. Chem. Commun.*, *25*, 2642, 1960.

41. Kyrš, M., J. Pelcik, and P. Polansky, *Colln. Czech. Chem. Commun.*, *27*, 155, 1962.

42. Kyrš, M. and S. Podesua, *Colln. Czech. Chem. Commun.*, *27*, 289, 1962.

43. Schulz, W. W. and T. R. McKenzie, *U.S. Patent* 2,982,785, 1961.

44. Wischow, R. P., U.S. AEC Report CF-61-3-141, Oak Ridge National Laboratory, Oak Ridge, TN, 1961.

45. Pummery, F. W. C. and J. H. Moss, United Kingdom Report AERE-R-3596, Atomic Energy Research Establishment, Harwell, UK, 1960.

46. Pummery, F. W. C. and J. H. Moss, United Kingdom Report AERE-R-3597, Atomic Energy Research Establishment, Harwell, UK, 1960.

47. Slater, L. M., *Nucl. Sci. Eng.*, *17*, 576, 1963.

48. Crowther, P. and F. L. Moore, *Anal. Chem.*, *35*, 2081, 1963.

49. Beard, S. J. and W. C. Schmidt, U.S. AEC Report HW-81092, General Electric Co., Richland, WA, 1964.

50. Larson, D. E., U.S. AEC Report ARH-564, Atlantic Richfield Hanford Co., Richland, WA, 1968.

51. Arnold, P. M. and L. C. Carpenelli, Jr., U.S. ERDA Report ARH-CD-917, Atlantic Richfield Hanford Co., Richland, WA, 1977.

52. Singh, S. P. N., U.S. DOE Report SD-RE-PCP-011, Rockwell Hanford Operations, Richland, WA, 1983.

53. Jones, Y. M., U.S. AEC Report BNWL-270, Pacific Northwest Laboratory, Richland, WA, 1966.

54. Baetsle, L. H., D. Van Deyck, D. Huys and A. Guery, Report EUR 2497, Centre d'Etude l'Energie Nucleaire, Mol, Belgium, 1965.

55. Aubertin, C. and J. Lefevre, *French Patent* 1,469,088, 1967.

56. Lefevre, J., French Report CEA-Conf. 1092, 1969.

57. Baetsle, L. H., D. Van Deyck, and D. Huys, *J. Inorg. Nucl. Chem.*, *27*, 683, 1965.

58. Bray, L. A., U.S. AEC Report HW-SA-2982, General Electric Co., Richland, WA, 1963.

59. Bray, L. A., *Nucl. Sci. Eng.*, *20*, 359, 1964.

60. Keder, W. E., E. C. Martin, and L. A. Bray, in *Solvent Extraction Chemistry of Metals*, H. A. C. McKay, T. V. Healy, I. L. Jenkins, and A. Naylor, Eds., MacMillan & Co., New York, p. 343, 1965.

61. Richardson, G. L., U.S. AEC Report HW-81091, General Electric Co., Richland, WA, 1964.

62. Smelov, V. S. and V. P. Lanin, *Sov. Radiochem. (Eng. Transl.)*, *16*, 181, 1974.

63. McDowell, W. J. and R. R. Shoun, "An Evaluation of Crown Compounds in Solvent Extraction of Metals," in *Proceedings ISEC 77*, B. H. Lucas, G. M. Ritcey, and H. W. Smith, eds, Canadian Inst. Mining Met., Montreal, Quebec, 1977.

64. Kinard, W. F., W. J. McDowell, and R. R. Shoun, *Sep. Sci. Tech.*, *15*, 1013, 1980.

65. Kinard, W. F. and W. J. McDowell, *J. Inorg. Nucl. Chem.*, *43*, 2947, 1981.

66. McDowell, W. J., B. A. Moyer, G. M. Case, and F. I. Case, *Solv. Extr. Ion Exch.*, *4*, 217, 1986.

67. Rais, J., P. Selucký, and M. Kyrš, *J. Inorg. Nucl. Chem.*, *38*, 1376, 1976.

68. Rais, J., E. Šebestova, P. Selucký, and M. Kyrš, *J. Inorg. Nucl. Chem.*, *38*, 1742, 1976.

69. Štefek, M., M. Kyrš, and J. Rais, *Zh. Anal. Khim.*, *31*, 1364, 1976.

70. Kyrš, M., L. Kadlecová, J. Rais, P. Selucký, J. Teplý, B. Ya. Galkin, R. I. Ljubcev, S. I. Rovnj, V. N. Romanovskii, N. S. Tichonov, and D. N. Shiskin, in *Proceedings of the IV Symposium, Karlovy Vary, Czechoslovakia, March 1977*, Vol. 1, p. 246, Czechoslovak Atomic Energy Commission, Prague, Czechoslovakia, 1977.

71. Ľ. Mátel, R. Cech, F. Macášek, S. Heřmánek, and J. Plešek, *Radiochem. Radioanal. Lett.*, *35*, 241, 1978.

72. Macášek, F., Ľ. Mátel, and M. Kyrš, *Radiochem. Radioanal. Lett.*, *35*, 247, 1978.

73. Selucký, P., P. Vaňura, J. Rais, and M. Kyrš, *Radiochem. Radioanal. Lett.*, *38*, 297, 1979.

74. Galkin, B. Ya., I. N. Lazarev, R. I. Ljubcev, V. N. Romanovskii, D. N. Shiskin, J. Rais, M. Kyrš, P. Selucký, and L. Kadlecova, *Proceedings of the Vth Symposium, Mariánské Lázne, Czechoslovakia April, 1981*, Czechoslovak Atomic Energy Commission, Prague, Czechoslovakia, 1981.

75. Koprda, V., V. Ščasnár, and P. Galán, *J. Radioanal. Chem.*, *80*, 55, 1983.

76. Kyrš, M. and J. Rais, "Separation of Fission Products by Solvent Extraction with Dicarbollide in Radioanalytical Chemistry and Technology", paper presented at *Separation of Ionic Solutes, SIS, 85 Conference, Smolenice, Czechoslovakia, September, 1985.*

77. Shuler, R. G., C. B. Bowers, Jr., J. E. Smith, Jr., V. Van Brunt, and M. W. Davis, Jr., paper submitted to *Solv. Extr. Ion Exch.*

78. Bray, L. A. and H. H. Van Tuyl, U.S. AEC Report HW-69534, General Electric Co., Richland, WA, 1961.

79. Richardson, G. L., U.S. AEC Report BNWL-4, Pacific Northwest Laboratory, Richland, WA, 1965.

80. Bray, L. A., L. F. Lust, R. L. Moore, F. P. Roberts, F. M. Smith, H. H. Van Tuyl, and E. J. Wheelwright, *Chem. Eng. Prog. Symp. Series, 60,* 9-19, 1964.

81. Bray, L. A., U.S. AEC Report HW-79286, General Electric Co., Richland, WA, 1963.

82. Van Deyck, D. and L. H. Baetsle, Belgium Report EUR 2748.2, Centre d'Etude de l'Energie Nculeaire, Mol, Belgium, 1966.

83. Davis, D. K., J. A. Partridge, and O. H. Koski, U.S. ERDA Report BNWL-2063, Pacific Northwest Laboratory, Richland, WA, 1977.

84. Wischow, R. P. and D. E. Horner, U.S. AEC Report ORNL-3204, Oak Ridge National Laboratory, Oak Ridge, TN, 1962.

85. Schulz, W. W. and G. L. Richardson, U.S. AEC Report HW-79762, Pts 1 and 2, General Electric Co., Richland, WA, 1964.

86. Schulz, W. W., J. E. Mendel, and G. L. Richardson, *Ind. Eng. Chem., Process Design Develop.*, *2*, 134. 1963.