Review and Assessment of Technologies for the Separation of Cesium from Acidic Media

R. J. Orth
K. P. Brooks
D. E. Kurath

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Pacific Northwest Laboratory
Richland, Washington 99352

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Summary

A preliminary literature survey has been conducted to identify and evaluate methods for the separation of cesium from acidic waste. The most promising solvent extraction, precipitation, and ion exchange methods, along with some of the attributes for each method, are listed in Table S.1.

The main criteria used in evaluating the separation methods were as follows:

- Good potential for cesium separation must be demonstrated (i.e., cesium decontamination factors on the order of 50 to 100 as discussed on p. 1.2).
- Good selectivity for cesium over bulk components must be demonstrated.
- The method must show promise for evolving into a practical and fairly simple process.
- The process should be safe to operate.
- The method must be robust (i.e., capable of separating cesium from various acidic waste types).
- Secondary waste generation must be minimized.
- The method must show resistance to radiation damage.

The most promising separation methods did not necessarily satisfy all of the above criteria, thus key areas requiring further development are suggested for each method. The report discusses in detail these and other areas requiring further development, as well as alternative solvent extraction, precipitation, ion exchange, and 'other' technologies that, based on current information, show less promise for the separation of cesium from acidic wastes because of significant process limitations. When appropriate, the report recommends areas of future development.

Table S.1. Promising Methods for Cesium Separation from Acidic Waste.

SEPARATION METHOD	ATTRIBUTES BASED ON AVAILABLE DATA	REQUIRED FURTHER DEVELOPMENT
SOLVENT EXTRACTION		
Crown ether + anion exchanger (organic)	<p>Good cesium separation.</p> <p>Shows potential for evolving into a practically viable process.</p> <p>Resistance to radiation damage has been indicated.</p> <p>Has undergone a fair amount of development.</p>	<p>Safety concerns exist regarding current diluents. Identify and test alternative diluent(s).</p> <p>Test on simulated and actual waste to better determine process robustness as related to Cs separation and selectivity.</p>
Cobalt dicarbide	<p>Good cesium separation.</p> <p>Good cesium selectivity over some bulk components.</p> <p>Shows potential for evolving into a practically viable process.</p> <p>Resistance to radiation damage has been indicated.</p> <p>Has undergone a fair amount of development.</p>	<p>Safety concerns exist regarding current diluents. Identify and test alternative diluent(s).</p> <p>Test on simulated and actual waste to better determine process robustness as related to Cs separation and selectivity.</p>
PRECIPITATION		
Phosphotungstic acid	<p>Good cesium separation.</p> <p>Shows potential for evolving into a practical process.</p> <p>Safe process to operate.</p> <p>Resistance to radiation damage suggested.</p> <p>Has undergone a fair amount of development.</p>	<p>Conduct additional tests for precipitations conducted in series to increase Cs separation.</p> <p>Waste Minimization: Determine the impact the precipitate will have on low level and high level waste.</p> <p>Test on simulated and actual waste to better determine process robustness as related to Cs separation and selectivity.</p>
Ferrocyanides (nickel, copper, iron)	<p>Good cesium selectivity over some bulk components.</p> <p>Shows potential for evolving into a practical process.</p> <p>Potential safety issue if ferrocyanides enter tank farm system.</p>	<p>Determine impact of precipitations conducted in series will have on Cs separation.</p> <p>Determine impact the precipitate will have on low-level and high-level waste.</p> <p>Test on simulated and actual waste to better determine process robustness as related to Cs separation and selectivity.</p>

Table S.1. (contd)

SEPARATION METHOD	ATTRIBUTES BASED ON AVAILABLE DATA	REQUIRED FURTHER DEVELOPMENT
ION EXCHANGE		
Ammonium molybdophosphate	<p>Good cesium separation.</p> <p>Good cesium selectivity over bulk components.</p> <p>Shows potential for evolving into a practical process.</p> <p>Resistant to radiation damage.</p> <p>Has undergone a fair amount of development.</p>	<p>Conduct further work on eluting characteristics.</p> <p>Identify satisfactory support systems.</p> <p>Identify potential prewash systems for improving exchanger selectivity.</p> <p>Test on simulated and actual waste to better determine process robustness as related to Cs separation and selectivity.</p>
Ferrocyanides	<p>Good cesium separation.</p> <p>Shows potential for evolving into a practical process.</p> <p>Resistant to radiation damage.</p> <p>Has undergone a fair amount of development.</p>	<p>Test hydrazinium to prevent oxidation on high capacity exchangers.</p> <p>Identify potential prewash systems for improving exchanger selectivity.</p> <p>Test on simulated and actual waste to better determine process robustness as related to Cs separation and selectivity.</p>
Crystalline Silico-Titanates	<p>Good cesium separation.</p> <p>Shows potential for evolving into a practical process.</p> <p>Good cesium selectivity over a wide range of conditions.</p> <p>Inorganic material; probably radiation resistant.</p> <p>Could also be used as a precipitant.</p>	<p>Production needs to be scaled up and powder needs to be formulated into particles usable in a column unless used as a precipitant.</p> <p>Method of eluting the material required unless a once through mode of operation is adopted.</p> <p>Additional tests on simulated and actual waste to determine process robustness as related to Cs separation and selectivity.</p> <p>A relatively new material with little published data available.</p>

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Nomenclature

AMP:	Ammonium molybdophosphate
ARHCO:	Atlantic Richfield Hanford Co.
CC:	Complex concentrate
CRADA:	Cooperative Research and Development Agreement
CE:	Crown Ether
CST:	Crystalline-Silico titanates
D_{Cs} :	Cesium solvent extraction distribution coefficient given as concentration in the organic phase divided by the concentration in the aqueous phase.
D_F :	Decontamination factor
HAW:	High Activity Waste
HDDNS:	Didodecyl-naphthalene sulfonic acid
HDEHP:	Di-(2-ethylhexyl) phosphoric acid
HDNNS:	Dinonyl-naphthalene sulfonic acid
HLW:	High Level Waste
HWVP:	Hanford Waste Vitrification Plant
INIS:	International Atomic Energy Agency
LLW:	Low Level Waste
MIBK:	Methyl Isobutyl Ketone
NTIS:	National Technical Information Service
ORNL:	Oak Ridge National Laboratory
PAA:	Polyantimonic acid
PTA:	Phosphotungstic acid
PUREX:	Plutonium Uranium Extraction
SLM:	Supported liquid membrane
SST:	Single-Shell Tank
TBP:	Tributyl phosphate
TiP:	Titanium phosphate
TRU:	Transuranic Elements
λ_d :	Nondimensionalized cesium ion exchange distribution coefficient; K_d (mL/g) multiplied by the bed density (g/mL). Also approximately equal to the bed volumes processed at 50% cesium breakthrough under certain column loading conditions.

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1.0 Introduction

1.1 Background

The Hanford Site in Washington State manages 177 underground storage tanks containing approximately 250,000 m³ of waste generated during past defense reprocessing and waste management operations. 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 the bulk of many radionuclides, such as transuranic (TRU) components and ⁹⁰Sr. Salt cake, generated by extensive evaporation of aqueous solutions, consists primarily of dried sodium salts. The supernates are concentrated (5-15 M) aqueous solutions of sodium and potassium salts. The salt cake and supernate contain most of the water-soluble radionuclides, such as ¹³⁷Cs, although significant amounts of cesium are present in the sludge.

Waste pretreatment plans, in general, involves separating the Hanford tank wastes into high-level waste (HLW) and low-level waste (LLW) fractions for final disposal. When this review was conducted, the plan for final disposal of the waste was to vitrify the HLW and to dispose of the LLW as a grout waste form. Current plans call for both the fractions to be converted to glass. It is anticipated that most of TRU components, ¹³⁷Cs, and ⁹⁰Sr will be vitrified with the HLW stream.

Several pretreatment options are currently being considered. A minimum pretreatment option involves washing the sludge to remove soluble components, followed by ion exchange to remove cesium from the supernate and wash solutions. Another involves considerable pretreatment to substantially decrease volume of glass: the sludge would be dissolved in nitric acid and the TRU components, ¹³⁷Cs, and ⁹⁰Sr would be separated from the bulk components in the dissolved sludge. The bulk components would be disposed of as LLW, and the TRUs, ¹³⁷Cs, and ⁹⁰Sr would be sent to the Hanford Waste Vitrification Plant (HWVP).

The more vigorous pretreatment approach requires the use of separation technologies that can effectively separate TRU components, ¹³⁷Cs, and ⁹⁰Sr, from acidified waste streams. Several candidate technologies for the separation of TRUs and Sr from the bulk components in the waste have been identified and are undergoing further development, and several well developed separation technologies exist for removing cesium from alkaline waste. However, the identification, assessment, and development of separation technologies for removing cesium from acidic solutions is required if cesium is to be effectively removed from acidified Hanford tank wastes.

1.2 Purpose and Scope

The purpose of this study is to identify and evaluate cesium removal processes that are potentially applicable to **acidified** Hanford waste streams. Promising technologies and further development requirements were identified through literature searches, journal reviews, and reviews of technical society conference proceedings as well as consultation with experts in the field. Literature searches included such databases as Energy Science and Technology Database, Energy Research Abstracts, Chemical Abstracts, Engineering Index, International Atomic Energy Agency (INIS) Atomindex, and National Technical Information Service (NTIS) Government Reports. Keywords, such as "cesium,"

were used in conjunction with "waste," "removal," "separation," "ion exchange," "solvent extraction," or "precipitation." Articles were restricted to those in English. The literature review was generally limited to published material.

Although the required decontamination factors (D_F)^(a) values for cesium are not known for each Hanford waste tank, average values are available. Analysis of the overall average composition of Hanford single-shell tank (SST) waste (Straalsund et al. 1992) suggests that disposal of the bulk components as low-level class A waste would require a minimum cesium D_F of 21. The reported cesium D_F s were for the total waste (supernate+solids) before acid dissolution. Normally, much of the cesium can be simply washed from the sludge. However, in some cases a significant fraction of the cesium cannot be removed simply by washing (Lumetta 1994). For this study it will be assumed that 10% of the total cesium is present in the solids, although the true value is highly variable. Thus, the required D_F for acid side processing would be 2.1. The sum-of-fractions-rule portion of the class A regulations and feed variability possibilities make it advisable that target D_F s be 10-fold greater than the minimum reported D_F values. Thus, a cesium D_F of approximately 21 for acid side processing of single-shell tanks can be calculated. Overall, the cesium decontamination requirements for the tank waste has been estimated at approximately 60. Thus, in assessing the various separation technologies, minimum required D_F s of 50 to 100 for cesium were considered.

In most cases, at least 1 M nitric acid will probably be required to dissolve the sludge; thus for this investigation, acidified waste was defined as having a pH < 2. This review excluded separation technologies restricted to a pH > 2.

Technology evaluation considered the presence of bulk components, such as sodium, iron, aluminum zirconium, zinc, and bismuth, as well as safety and health issues, process simplicity, and the impact of the product streams on the vitrification plant and on low-level grout.^(b)

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- (a) The decontamination factor is defined as the cesium concentration in the original feed divided by the cesium concentration in the effluent after processing.
- (b) The low-level waste form was recently changed from grout to glass. (Hanford Federal Facility Agreement and Consent Order 1994).

2.0 Cesium Separation Technology Assessment

Potential technologies for the separation of cesium from acidified waste streams include solvent extraction, precipitation, ion exchange, and other alternatives. For each separation technology, the pertinent literature relating to potentially viable systems is listed in tables, arranged chronologically to facilitate following the development sequence. The tables also include pertinent separation data, the experimental conditions, and additional comments for each source. The text describes the advantages and limitations of each system, and each section concludes with suggestions for further development of the separation technique.

2.1 Solvent Extraction

Only two solvent extraction systems currently show any promise in separating cesium from acidic wastes (Schultz and Bray 1987; Reilley, Mason, and Smith 1990; Kolarik 1991; Gerber 1992): crown ethers or cobalt dicarbollides.

2.1.1 Crown Ethers

Investigations into use of crown ethers (CE) for the extraction of cesium from acid waste streams (see Table A.1 in the Appendix) have focused on use of various solvents, additives, and crown ethers to enhance extraction. A tributyl-phosphate, kerosene, and crown ether system failed to significantly extract cesium, regardless of which crown ether was used (Gerow and Davis 1979; Gerow, Smith, and Davis 1981). However, adding organic soluble anions to the mixture increased the extraction of cesium as much as 100-fold. This increase was attributed to the notion that the organic soluble anion acted as a liquid ion exchanger, complexing with the cesium ion, making it more soluble in the organic phase, thus enhancing its complexation with the crown ether. The primary organic soluble anions used in these studies were HDEHP, HDNNS, and HDDNS.

Although the presence of HDEHP significantly enhanced the extraction of cesium, the distribution coefficient values are still too low for practical use in acidic waste. Use of HDEHP as the liquid ion exchanger is reasonable only at $\text{pH} > 1$ and is ineffective at higher acidities (Gerow and Davis 1979). Results were similar when HDEHP was added to a crown ether-benzene system (Kinard and McDowell 1981).

The use of HDDNS or HDNNS rather than HDEHP as the liquid ion exchanger allows the extraction of cesium at higher HNO_3 concentrations. For example, a D_{Cs} of 3.0 was obtained at 3M HNO_3 with a mixture of tributyl phosphate HDDNS, kerosene, and crown ether. The D_{Cs} was at a minimum in $\text{pH} 0.4$, which would allow stripping of the cesium from the organic phase.

Another study using HDDNS (Shuler et al. 1985) yielded similar cesium separation results. However, the distribution coefficients for zirconium and cesium were essentially the same. This was attributed to the extraction of zirconium by tributyl phosphate. Addition of a complexing agent such as oxalic acid to the aqueous phase may help minimize zirconium extraction. The D_{Cs} value was much higher ($D_{\text{Cs}} = 5.6$) when the crown ether concentration was increased to 0.1 M . Although this D_{Cs} is sufficiently high to reduce the effects of zirconium competition and provide proper D_{F} values, the

solubility of the crown ether at this high concentration may be questionable. The solubility of 4,4'(5') (1-hydroxy-2-ethylhexyl)benzo-18-C-6 in a 27% tributyl phosphate + 68% kerosene + 5% HDNNS should be investigated further. If solubility is not a problem and the effects of interfering ions can be reduced, this solvent extraction system may be a candidate for use at Hanford.

HDNNS and HDDNS have been added to other solvents, such as toluene, to enhance the extraction of cesium from acidified wastes (McDowell et al. 1986, Lumetta et al. 1991). In both of these studies D_{Cs} values were favorable, but the addition of sodium (1M to 4 M) led to a significant decrease in the extraction of cesium (Lumetta et al. 1993). Use of this system at Hanford would require that sodium be removed before extraction of cesium. A further drawback is the low flash point of toluene.

Dietz and Horwitz (1990) found that the poor solubility of crown ether in octanol severely limited the extraction of cesium. Crown ether was more soluble in methyl isobutyl ketone (MIBK), and use of that solvent increased the D_{Cs} approximately 6-fold. However, MIBK also has a low flash point (13°C). Flattening of the extraction curve at the stripping end suggests that stripping would be difficult with octanol or MIBK as the solvent. The authors suggested that 0.1 M H_2SO_4 would efficiently strip the cesium; however, only limited amounts of sulfate can be tolerated in the feed to the vitrification process.

In the same study, the cesium distribution coefficient increased with the water content of all the 21 diluents that were tested (alcohols, ketones, carboxylic acids, and esters). The authors recommended 1) screening of other diluents to identify one with a water content similar to that of MIBK but possessing more desirable physical properties (e.g., higher flash point), 2) examining other crown ethers, such as the mono-benzo analog of DCH18C6 or a dibenzo-compound having alkyl groups other than t-butyl, for greater solubility in octanol, and 3) evaluating the effect of hydrophobic counterions.

Use of $H[SbCl_6]$ as an ion exchanger yielded one of the largest D_{Cs} (Blasius and Nilles 1984). Unfortunately, this system required highly toxic and flammable polar solvents, such as nitrobenzene or nitroethane, to dissolve the liquid ion-exchangers that were used.

2.1.2 Cobalt Dicarbolides

Several groups have investigated the use of cobalt dicarbolidides for the extraction of cesium from acid waste streams (HNO_3) (see Table A.2 in the Appendix). Cobalt dicarbolidide as an extractant for the separation of cesium or strontium generally yields higher D_{Cs} values than the crown ethers. All of the studies yielded favorable D_{Cs} values for HNO_3 concentrations up to 1.0 M. However, these high values could be achieved only when the solvent was nitrobenzene (Rais et al. 1976). The solubility of cobalt dicarbolidide was comparable in tributyl phosphate and nitrobenzene; however, the limited cesium distribution data indicate that cesium did not extract as well into the tributyl phosphate system. Additional tests with tributyl phosphate would be useful.

Several of the articles noted that cesium extraction decreased with increasing acid concentration (Rais et al. 1976, Scasnar and Koprda 1978, Koprda and Scasnar 1979, Scasnar and Koprda 1980) and that the selectivity for cesium over other fission products either increased or stayed the same with increasing acid concentration (Scasnar and Koprda 1978, Koprda and Scasnar 1979, Scasnar and Koprda 1980). In particular, selectivity for cesium over zirconium increased with increasing HNO_3 concentration.

In a comparison of cesium separation by cobalt ferrocyanide, copper ferrocyanide, ammonium molybdophosphate ion exchangers, and the cobalt dicarbolidate extraction system under acidic conditions, the cobalt dicarbolidate system was much more selective for cesium than for other fission products (e.g., zirconium), while showing only slightly lower extraction values for cesium in batch contacts (Scasnar and Koprda 1980).

Testing the premise that chlorinated dicarbolidate may give a more stable Cs-dicarbolidate complex, Koprda and Scasnar (1979) and Scasnar and Koprda (1980) found that cesium extraction was essentially the same regardless of which cobalt dicarbolidate was used. However, the chlorinated cobalt dicarbolidate derivative may permit simultaneous extraction of strontium and cesium (Reilly, Mason, and Smith 1990).

Romanovskii and colleagues (1992) used chlorinated cobalt dicarbolidates to separate cesium from acidic waste at nitric acid concentrations of 0.5 M to 5.0 M. As acid concentration increased, cesium extraction decreased significantly, and when the cesium concentration was increased to approximately 0.1 M, the D_{Cs} decreased dramatically at all the acid concentrations tested (at a chlorinated cobalt dicarbolidate concentration of 0.097 M).

In a review article, Kolarik (1991) noted that a Russian group used cobalt dicarbolidate and its chlorinated derivative to separate 99.8% and 98% ^{137}Cs , respectively, from an actual high-activity waste (HAW) solution in a hot counter-current test; Esimantovskii et al. (1992) published similar results. Alfonin et al. (1990) reported a D_F of 2×10^4 when using a chlorinated derivative of cobalt dicarbolidate to separate cesium from an actual HAW solution in a hot counter-current pilot test but did not report the number of stages required.

One deterrent to using cobalt dicarbolidate for the separation of cesium or strontium is the requirement for nitrobenzene as a solvent. Nitrobenzene is on the EPA "Extremely Hazardous" list (Lewis 1991) because of its toxicity and potential for explosion in strong acids and bases. The high cost of cobalt dicarbolidate may be a drawback, although material costs are generally a minor concern relative to the total plant operating cost.

2.1.3 Suggested Future Development

The suggestions for future development required to make the two solvent extraction systems practically viable are given in a stepwise manner, so that one successful development step leads to the next.

- Identify alternative practical diluents for the cobalt dicarbolidate and crown ether systems.

For both solvent extraction systems, under certain conditions, cesium extraction values have been sufficiently high to make the systems potentially viable for treating cesium-containing acidified waste. The key is to identify diluents that can be safely used in the extraction processes while maintaining high extraction and selectivity for cesium. High extraction requires a solvent with high solubility for the extractant. For the cobalt dicarbolidate system, the solubility of cobalt dicarbolidate is an important factor in achieving high cesium extraction. Similar concerns prevail for the crown ether systems. As suggested, it may be useful to study solubilities in both systems. Their distribution coefficients may be increased by simply increasing the extractant concentration to the solubility level.

It appears that polar solvents are not necessary in crown ether systems. However, the most promising results thus far were obtained with toxic and flammable solvents, such as toluene or MIBK. Thus, alternative solvents must be identified if these systems are to have practical use.

- Investigate the degree of extraction of other elements in both solvent extraction systems.

The solvent must have a relatively low affinity for the bulk components. Thus, additional laboratory data on the extraction of such elements as Na, Fe, K, Zr, Zn, Ca, Bi, Sr should be obtained under various conditions (e.g., pH). This will also aid in determining the best scrub solutions and the number of scrub stages required. For example, a crown ether system containing tributyl phosphate extracted appreciable quantities of zirconium; therefore, an additive such as oxalic acid may be required to prevent the zirconium extraction.

- Investigate the stripping capabilities of the cobalt dicarbonyl and crown ether systems.

Most studies thus far have focused on the extraction of cesium but have not dealt in detail with stripping cesium from the organic phase once it is loaded.

- Investigate the degree of chemical and radiolytic degradation in the two systems.

The literature suggests that both systems are resistant to radiolytic degradation; however, only limited data are available. Furthermore, chemical degradation due to solvent contact with the acidic solutions during the extraction and an inability to strip certain components may cause problems in the overall process.

- Develop a flowsheet using batch testing of actual waste for the cobalt dicarbonyl and crown ether systems.

To date, most testing has used simulated wastes prepared in the laboratory. Batch laboratory tests will be required to evaluate each system's performance on actual waste. A solvent extraction flowsheet is needed for each waste type of interest.

- Conduct counter-current contact tests on simulated and actual wastes.

Bench scale counter-current testing will be required to confirm and develop the process chemistry flowsheets for use in pilot-scale and large systems.

2.2 Precipitation

Currently, three precipitation methods can possibly be used to separate cesium from acidified waste streams (see Tables A.3, A.4, and A.5 in the Appendix). Recent review articles have addressed some of the studies to be discussed (Schultz and Bray 1987, Kolarik 1991, Gerber 1992).

2.2.1 Alum

Alum co-precipitation was used at the Oak Ridge National Laboratory (ORNL) to separate cesium for commercial use (Rupp 1955). Since the goal was commercial use, purity rather than yield was of primary importance. In the published flowsheet for the removal of ruthenium, rare earths, strontium, and cesium, co-precipitation of cesium with ammonium alum or potassium alum followed removal of the other elements. In one batch contact, over 99% of the cesium was removed from solution. The author suggested that the cesium co-precipitation process might precede removal of other elements. The exact pH during the co-precipitation process was not reported, simply that a pH 2.5 solution was acidified. The presence of sulfate in the cesium-alum precipitate is not desirable in vitrification. Barton et al. (1958) noted that cesium alum precipitates are bulky and non-selective.

2.2.2 Ferrocyanides

Ferro- and ferricyanides have been primarily used on alkaline wastes. Like the cesium-alum process, precipitation of cesium by ferro- or ferricyanides was done primarily in the late 1950s and 1960s to recover cesium for use in industry.

The most promising of these processes appear to be nickel, copper(II), and iron (III) ferrocyanides (Barton et al. 1958, Van Tuyl and Moore 1959). Nickel ferrocyanide yielded the best combined recovery and the smallest volume of precipitate in batch tests of unconcentrated wastes. Uranium and iron interfere with the nickel ferrocyanide precipitation of cesium. This precipitation process was insensitive to sodium nitrate concentrations up to 0.4 M and HNO₃ concentrations of 0.1 M to 3 M; addition of ammonium ion tended to enhance cesium recovery. Copper (II) and iron (III) ferrocyanides yielded comparable D_F values but larger precipitate volumes. Of the ferricyanides, only the nickel compound yielded an appreciable D_F. Radiolytic degradation was minimal in all ferri- and ferrocyanide precipitation systems.

2.2.3 Phosphotungstic Acid

The precipitation of cesium with phosphotungstic acid (PTA) was first proposed in connection with Hanford PUREX acid waste by H. H. Van Tuyl in 1963. The process steps were defined by Beard and Schmidt (1964) and carried out in the PUREX head-end centrifuges. As was the case with other early precipitation, the prime objective of recovery for commercial use put the emphasis on purity rather than yield. The early flowsheet consisted of 5 steps: 1) centrifugation to remove already precipitated compounds, 2) precipitation of cesium by adding a slight excess of phosphotungstic acid, 3) centrifugation to remove the precipitate from the supernate, 4) cake wash, using 1 M HNO₃ to provide additional decontamination from other fission products, and 5) cake removal by dissolving in 1 M NaOH. The D_F was 50, and phosphotungstic acid represented 97% of the total chemical cost.

Bray and Larson (1968) investigated and Larson and Smith (1969) worked out the process steps. Larson and Smith reported that a single precipitation could routinely recover 98% of the cesium. Arnold and Carpinelli (1977) re-evaluated the process for the Atlantic Richfield Hanford Co. (ARHCO) and "... concluded that the PTA process offered a feasible and proven method for recovery from PUREX current acid waste." In 1983, Singh evaluated the PTA process for the Rockwell Hanford Operation Co., reconfirming the ARHCO evaluation.

A follow-up study was conducted to select a reference process for partially decontaminating West Valley **alkaline** waste by removing cesium (Bray et al. 1984). They compared four technologies: zeolite inorganic ion exchange (Ionsiv IE-95), organic ion exchange (Duolite CS-100), sodium tetraphenylboron precipitation, and phosphotungstic acid precipitation. The application of the PTA process required acidification of the alkaline waste.

With regard to safety and health considerations, equipment and process complexity (process reliability), process impacts on the waste vitrification system and low-level waste, and process performance, the phosphotungstic acid precipitation method was ranked second, slightly behind the inorganic ion exchange process. The phosphotungstic acid process is more complex than inorganic ion exchange (i.e., requires more batch operations) and the low-level waste produced contains large quantities of added chemicals. Phosphotungstic-acid precipitation required that the alkaline West Valley wastes be acidified, and then the supernate had to be neutralized before being sent to the low-level waste-treatment facility. Treatment of acidic waste, as in the case addressed by this report, would simplify the process and less salt would be sent to the low-level waste-treatment facility.

Additional laboratory-scale work indicated that a D_F of approximately 50 could be obtained in one contact at a 1:1 molar ratio of phosphotungstic acid to cesium. Treating the supernate from that contact with the same amount of phosphotungstic acid consistently yielded an overall D_F of 10^4 . One contact with a 2:1 molar ratio of phosphotungstic acid to cesium yielded a D_F of approximately 177. Thus, two precipitations in series were more effective than one precipitation with an equivalent amount of phosphotungstic acid. Furthermore, for a given phosphotungstic acid to cesium ratio, higher nitric acid concentrations resulted in higher D_F values; the range of nitric acid concentrations studied was 0.3 M to 1.5 M.

When the system operated at 60°C, the required contact time was drastically shorter (3 minutes) than at 25°C (15 minutes). The resulting precipitate had a particle diameter of 10 to 50 microns. Water washing of the particles yielded 0.3 to 1.3 micron particles; therefore water washing should be avoided. Filtering tests using one 60"-long Mott filter unit with a surface area of 0.06 m² and a 0.5 micron porous metal filter element yielded a D_F of 4×10^4 .

Lumetta et al. (1993) conducted laboratory-scale tests on synthetic Hanford Complex Concentrate (CC) wastes. Nearly stoichiometric amounts of sodium phosphotungstate and cesium were present in approximately 1 M HNO₃; the first contact yielded a D_F of 88.7. A second contact with the same amount of sodium phosphotungstate added yielded an overall D_F of 1300.

In testing the use of phosphotungstic acid to remove cesium from simulated 1-AW MTR liquid waste, Grossi, Pietrelli, and Troiani (1992) found that a reaction time of 14 hours was required to obtain a $D_F > 100$. Centrifugation and filtration of the precipitant yielded similar D_F values for the 14-hour contact time; for <2.5-hour contact times, centrifugation resulted in D_F values at least twice those of filtration.

When precipitation was conducted at 50°C rather than 25°C, D_F values were much lower for the reaction times tested (1, 1.5, 2.5, and 14 hours). Enhanced solubility of PTA-Cs at 50°C has a greater effect than does temperature on reaction kinetics. Bray, Wise and Meyers (1984 unpublished) had contrary results, although their study used higher Cs and PTA concentrations and tested a different waste.

2.2.4 Suggested Future Development

To date, among the precipitation processes for removing cesium from wastes, phosphotungstate precipitation has undergone the most development. Ferrocyanide (nickel, copper, or iron) precipitation appears to be the next most attractive processes. Only limited data exist regarding alum and ferrocyanides precipitation processes for the treatment of acidic waste streams. Ferrocyanides and alum effectively separate cesium from acidified waste; however, the alum precipitate is bulky, and entry of ferrocyanides into the tank farm system would present a safety hazard.

The following recommendations are given in a stepwise manner, with one successful development step leading to the next.

- Conduct laboratory testing on simulated waste, using phosphotungstic acid, nickel, copper and iron ferrocyanides, and alum as precipitants.

The resultant data would permit comparison of D_F values for cesium removal by the different precipitation methods. Investigation should encompass such variables as precipitate volume, acid concentration, temperature, mixing time, precipitate particle size, precipitate settling and filterability, as well as the impact of successive contacts (particularly for the ferrocyanide and alum systems). The precipitation of other elements (e.g., Na, Fe, Zn, Zr, Ca, Bi) from the waste should also be evaluated to determine 'separation factors.'

- Evaluate the impact of the generated precipitate on the glass plant and that of the supernate on the low-level waste. Investigate potential safety risks associated with the ferrocyanides and their potential to enter the tank farm system.

For example, the presence of sulfate ion in the feed to the glass plant is undesirable. If the alum process would send an unacceptable quantity of sulfate ion to the vitrification plant, processes for converting the cesium to a non-sulfate form should be investigated. The high sulfate load may ultimately eliminate the alum process from consideration. Similar evaluations should be conducted for the ferrocyanide and phosphotungstic acid processes:

- Investigate the degree of chemical and radiolytic degradation for each precipitation process.
- Develop flowsheets from results of laboratory tests on actual waste for each process.
- Conduct larger scale filtering tests for each process.

2.3 Ion Exchange

Ion exchange processes are attractive for removing trace contaminants from a process stream. First, ion exchange is a relatively simple unit operation, requiring less maintenance and control than other separation techniques. Second, a relatively small amount of exchanger can process a large quantity of waste. For these reasons, ion exchange has been investigated for the removal of cesium from acidic wastes.

Four groups of exchangers have potential use in the removal of cesium from acid wastes: ferrocyanides, phosphates, oxides, and 'others'. They are almost exclusively inorganic, with the exception of macrocyclic ligands in the 'others' category. The many organic exchangers for removal of cesium from alkaline waste will not be discussed.

The following variables may affect the effectiveness of ion exchange resins:

- Exchange capacity
- Selectivity for cesium over competing ions
- Elution and regeneration characteristics
- Kinetics
- Solubility in acidic media
- Resistance to radiation damage.

Inorganic exchangers are stable with respect to radiation; therefore, this issue will not be addressed here. Each of the other issues for which literature information is available will be addressed,

2.3.1 Ferrocyanides

The use of ferrocyanides as ion exchangers is well established in the nuclear industry (Jacobi and Streat 1990). The literature addresses molybdenum, tungsten, zinc, titanium, cadmium, nickel, cobalt, and copper ferrocyanides, alone or in certain combinations.

These exchangers generally have reasonably good capacity at a concentration of 1M HNO_3 , improving as hydrogen ion concentration falls (see Table A.6 in the Appendix). Generally, at higher acid concentrations ($> 1\text{M H}^+$), iron oxidation causes a loss of capacity in the exchanger. For example, the capacity of zinc ferrocyanide decreases from 115 mg/g in neutral solution to 7 mg/g in 3M HNO_3 (Filippov et al. 1992).

Copper and molybdenum ferrocyanides show promise with respect to capacity, decontamination factor, kinetics, and selectivity for cesium. However, they dissolve in 0.5 to 1.0 molar acid more readily than other ferrocyanides. In molybdenum ferrocyanide, for example, acid not only oxidizes the iron, it breaks the matrix and the exchanger falls apart. Tungsten ferrocyanide is fairly insoluble in acid but has half the capacity of molybdenum ferrocyanide. Copper ferrocyanide undergoes a 7 to 20% weight loss at higher acid concentrations (Lee and Streat 1983). Similar trade-offs with all ferrocyanides make it impossible to single out one as much better than the others.

Molybdenum ferrocyanide has another disadvantage. Any nickel ion in the waste forms acid-insoluble deposits in the exchanger pores, preventing elution of cesium from the exchanger (Baetslé et al. 1973).

Tanihara (1991) found that the addition of trace amounts of hydrazinium or amidosulfate ion prevents oxidation at high acid concentrations, thereby increasing the distribution coefficient (K_d) by several orders of magnitude: from 10^3 to 10^8 mL/g for cobalt ferrocyanide and from 10^2 to 10^5 mL/g for copper ferrocyanide. The ferrocyanides with higher K_d values are often less selective for cesium.

Ferrocyanides exhibit poor selectivity for cesium in the presence of competing ions, such as the alkali metals, ammonium, iron, zirconium, zinc, and cobalt. Cobalt and copper ferrocyanides, for example, are selective for Zr, Zn, and Co as well as cesium (Scasnar and Koprda 1979). Molybdenum ferrocyanide removed cerium, zirconium, and niobium from a cesium-laden wasteform (Szlaurova et al. 1979).

2.3.2 Phosphates

Similar to the ferrocyanides, the phosphates also have reasonably high capacities (see Table A.7 in the Appendix). In extensive bench-scale testing, the phosphates show promise similar to the ferrocyanides, but they have not been established on a large scale.

Ammonium molybdophosphate (AMP) shows more promise than the other phosphates. It has very fast kinetics, high capacity, and a high distribution coefficient. It also has high capacity over a wide range of salt concentration and pH (Faubel and Ali 1986).

The primary disadvantages of AMP for use in columns are difficult elution and its microcrystalline structure. Elution requires high concentrations of ammonium ion. Sebesta and Stefula (1990) showed that AMP can be 92% eluted with 10 column volumes of $5M$ NH_4^+ . Suss and Pfrepper (1981) required 56 column volumes of $7.9M$ NH_4^+ to elute 80% when they used a porous polyacrylonitrile support rather than forming AMP-precipitate beads, thereby exposing a greater fraction of the exchanger to the high concentration eluant, allowing faster and more complete cesium removal.

Removal of the cesium from the AMP exchanger may well be important to its viability at Hanford. If AMP cannot be eluted, it may have to be vitrified with the cesium. HWVP specifications do not permit large quantities of phosphorus in the feed, and many of the tanks slated for cesium removal are above the phosphorus limits now.

Several approaches have been taken to improve the physical characteristics of AMP for use in columns. Many early attempts to put AMP on supports resulted in a loss in selectivity, capacity, and kinetics of the exchanger. More recent attempts claim more success. Min and Zhaoxiang (1992) combined AMP and titanium phosphate to improve elution and column stability. Faubel and Ali (1989) designed a modified suspended-bed column, in which the micro-crystalline AMP is allowed to lie loosely on porous substrate. No exchanger was lost, but they made no attempt to elute the resin.

Unlike AMP, zirconium phosphate can be eluted with $2M$ HNO_3 . However, it does not load cesium as effectively at higher acid concentrations, and it has much slower kinetics. At $1M$ HNO_3 , zirconium phosphate has a distribution coefficient of 10 to 150 mL/g versus 10^4 to 10^5 mL/g for AMP (See Table A.7 in the Appendix). Zirconium phosphate is also less selective than AMP. This exchanger's capacity is significantly reduced in the presence of sodium, cerium, and zirconium (Suss and Pfrepper 1981; Beaven et al. 1988).

Titanium phosphate, although its capacity and selectivity are lower than those of AMP, is an improvement over zirconium phosphate. Jones (1966) and Baetsle et al. (1973) obtained reasonably good loading in 2M HNO₃. Loading is strongly inhibited by increased sodium concentration.

Further study with phosphates should probably center on AMP exchangers. An attempt should be made to determine the best support system and elution scheme for the waste streams to be studied. If the column support issue can not be overcome, it may be advisable to test AMP in a precipitation process.

2.3.3 Oxides

Unlike the ferrocyanides and phosphates, none of the oxides show much promise (see Table A.8 in the Appendix). Manganese and titanium oxide did not effectively remove cesium from 1M HNO₃ (D_F = approximately 1). Antimony pentoxide's reasonable capacity in acid concentrations drops off quickly with the addition of sodium ion. In addition, it has slower kinetics than ferrocyanides and phosphates.

2.3.4 Others

The 'others' category includes polyantimonic acid, macrocyclic ligands, and zeolites. These exchangers show little potential (see Table A.9 in the Appendix).

Polyantimonic acid removes strontium from acidic media reasonably well but it has slow kinetics and a low capacity for cesium.

Macrocyclic ligands (Bradshaw et al. 1989) appear to be chromatographic rather than true ion exchangers. Tests at the Hanford site (Camaioni et al. 1992) have shown that more liquid is required to elute the exchangers than can be loaded on the column, thus not reducing the quantity of waste. Researchers at IBC Advanced Technologies claim recent significant improvements but have not yet published results.

Crystalline-Silico titanates (CSTs) are being developed at the Sandia National Laboratory for the treatment of alkaline waste. Recent work (Bray 1993) suggests that the material will be difficult to elute with nitric acid because K_d is high over a wide range of pH, nearly 3000 mL/g in 1 M nitric acid. CSTs therefore have a significant potential for removing cesium from acidified wastes. Sandia National Laboratory through a Cooperative Research and Development Agreement (CRADA) with the UOP company is working on a pellet formulation. This promising material is quite new and requires much development.

Zeolites have been studied in acidic solution with marginal success. Capacities for the different types of zeolites and acid conditions range from 4.3 to 158 mg/g. However, their kinetics tend to be slow, and zeolites dissolve in acid.

2.3.5 Suggested Future Development

The relative simplicity of ion exchange processes makes them easier to control and maintain than other more complex unit operations to separate cesium from acid waste. The limited available

literature suggests that CSTs are probably the most promising, followed by AMP, ferrocyanides (when stabilized with hydrazinium) and other phosphates (see Table A.10 in the Appendix). Silico-titanates show the greatest promise in removal of cesium from acid solutions if reuse of the material is not required.

As before, the suggested future developments are listed in a stepwise manner, so that one successful development step leads to the next.

- Conduct batch testing on simulated or actual acidified sludge to determine the selectivity of the exchanger for cesium in the presence of reasonable concentrations of competing ions.
- Identify potential prewash systems for improving exchanger selectivity.
- Study the potential for improving resin stability and capacity with additives (such as hydrazinium) and improved microporous polymeric supports.
- Investigate approaches to elution that will minimize waste produced and regenerate the column to its full potential.
- Develop a flowsheet using the most appropriate exchanger material to determine the impact on high- and low-level waste feeds.
- Conduct continuous column operations to understand and simulate the kinetics of the ion exchange process.
- Verify key results with tests on actual acidified sludge.

2.4 Other Cesium Separation Methods

Some methods other than conventional solvent extraction, precipitation or ion exchange can potentially be used to separate cesium from acidified waste streams (see Table A.11 in the Appendix).

2.4.1 Supported Liquid Membranes

The use of supported liquid membranes (SLM) for metals separation is basically an extension of solvent extraction. The membrane usually consists of a polymeric support material impregnated with the organic phase (extractant and diluent) and interposed between two aqueous solutions. Conditions in the aqueous feed solution (initially containing all of the metals) favor transfer of the metal(s) from the aqueous phase into the supported liquid membrane (i.e., extraction into the organic phase). Conditions in the aqueous phase on the other side of the membrane favor transfer of the metal(s) from membrane (i.e., stripping of the organic phase).

The potential advantages of supported liquid membrane separation are as follows: 1) high selectivities 2) ion transfer against the gradient, 3) use of small quantities of expensive extractants, 4) high separation factors in a single stage, and 5) concentrate product by use of high feed to strip-volume ratios. The potential disadvantages are physical and chemical membrane instability and membrane

plugging by solids. Some of the factors influencing membrane stability have been identified (Danesi et al. 1987). In 1984, Danesi published a detailed description of supported liquid membranes, referring to studies in which they have been used to recover copper, uranium, chrome, cobalt, and nickel.

Ramadan and Danesi (1988) studied the transfer rate and separation of strontium and cesium by supported liquid membranes using synergized crown ether carriers (see Table A.11 in the Appendix). Although they obtained a low D_F for cesium, the same conditions yielded a high D_F for strontium. The crown ether they used favors the extraction of strontium; thus, an alternative crown ether (see Table A.1) might yield higher cesium D_F values.

2.4.2 Electrochemical Ion Exchange

In electrochemical ion exchange, an applied potential controls the adsorption and elution behavior of the ion exchange material, which normally is bound to the electrode structure. For a weak-acid cation exchanger, application of a negative potential to the electrode will cause cations to adsorb rapidly onto the ion exchange material. On polarity reversal, the adsorbed cation(s) can be eluted into a relatively small volume of aqueous phase. The potential advantages of electrochemical ion exchange are 1) enhanced adsorption kinetics, 2) wide operable pH ranges, 3) adsorption approaching the ion exchanger's theoretical capacity while maintaining large D_F values, 4) addition of chemicals for regeneration not required, 5) mechanical support of ion exchange material by the electrode. Additional information on electrochemical ion exchange is available (e.g., Turner et al. 1988, Lain 1988, Turner et al. 1987, Turner et al. 1985).

The most promising electrochemical ion exchange system uses zirconium phosphate as the ion exchanger (Turner et al. 1987). Unfortunately, this system operates in alkaline media (see Table A.11 in the Appendix). AMP, a possible acid-media ion exchanger, turned out to be unstable under electrochemical conditions, causing precipitates to form during testing of the electrodes.

2.4.3 Electrodialysis

In electrodialysis, an electrochemical driving force separates ions: the negatively charged ions migrate toward the anode and the positively charged ions migrate toward the cathode. Ions of like charge can be separated by use of membranes that are selective for one ion over the other.

Gurski and Moskvina (1987) reported separation coefficients of 1 to 1.9 in a study of electrodialysis to separate cesium from sodium in an alkaline solution.

2.4.4 Suggested Future Development

These "other" processes require a substantial amount of further testing and development to determine if they have any potential for separating cesium from acidic wastes, particularly in comparison to the solvent extraction, precipitation, and ion exchange methods. Thus, only laboratory-scale development is discussed for the alternative cesium separation methods.

For the supported liquid membrane process, different membrane systems should be investigated, such as some of the crown ether systems. Membrane stability and plugging by solids are key issues.

For the electrochemical ion exchange method, alternative ion exchange media (see section 2.3) should be tested for stability and performance in acidic media.

For electrodialytic separation, membranes having high selectivities for cesium in acidic media should be identified and investigated; for example, membrane plugging by solids.

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Appendix A

Tabular Summary of Literature Survey

Table A.1. Solvent Extraction: Crown Ethers

Literature Source	Experimental Conditions	$D_{Cs}^{(a)}$	Comments
Gerow and Davis (1979)	25% Kerosene, 25% TBP, 50% HDEHP, 0.02 <u>M</u> 4,4'(5')-di-tert-butylbenzo-24-C-8, 0.001 <u>M</u> $CsNO_3$, pH=3.5-4.5	1.1	Efficiently stripped at pH > 1. No significant extraction without HDEHP. Extraction occurs only at relatively low acid concentrations.
Gerow et al. (1981)	68% Kerosene, 27% TBP, 5% DNS, 0.02 <u>M</u> bis-(4,4'(5')-[1-hydroxyheptyl]-benzo)-18-C-6, 0.001 <u>M</u> $CsNO_3$, 3.0 <u>M</u> HNO_3	2.0	At pH=0.4 can be stripped with minimal extraction. No significant extraction without DNS. Decreasing TBP concentration decreases D_{Cs} . D_{Cs} lower with HDEHP than with DNS at experimental conditions given.
Kinard and McDowell (1981)	0.125 <u>M</u> HDEHP, 0.25 <u>M</u> dicyclohexo-18-C-6, Benzene, 10^{-4} <u>M</u> $CsNO_3$, pH=4.0	0.27	Presence of HDEHP increased extraction by 100X. Benzene not a desirable solvent.
Blasius and Nilles (1984)	0.007 <u>M</u> $H[SbCl_6]$, 0.011 <u>M</u> dibenzo-21-C-7, 1,1,2,2-tetra-chloroethane, 4 ppm Cs, 1.0 <u>M</u> HNO_3	226	Polar solvents required to dissolve organic phase liquid ion exchangers. Nitroethane, nitrobenzene also tested as solvents. $Na[SbCl_6]$, $K[SbCl_6]$ also tested as liquid ion-exchangers.
Myasoedova et al. (1987)	0.05 <u>M</u> dicyclohexyl-24-C-8, tetrachloroethane, 0.05 <u>M</u> $CsNO_3$, 3.0 <u>M</u> HNO_3	0.079	D_{Cs} even lower when DCH18C6 used instead of DCH24C8.

Table A.1. (contd)

Literature Source	Experimental Conditions	$D_{Cs}^{(a)}$	Comments
Shuler et al. (1985)	5% NNS, 27% TBP, 68% kerosene, 0.05 <u>M</u> 4,4'(5') (1-hydroxy-2-ethylhexyl) benzo-18-C-6, 0.006 <u>M</u> Cs, 3.0 <u>M</u> HNO_3	1.6	Higher D_{Cs} values reported for higher crown ether concentrations, e.g., $D_{Cs} = 5.6$ at 0.1 <u>M</u> CE. Need to know solubility of this CE in TBP+kerosene. For experimental conditions given $D_{Zr} = 1.5$; therefore poor separation of Zr and Cs.
McDowell et al. (1986)	0.1 <u>M</u> HDDNS, 0.05 <u>M</u> di-tert-butylbenzo-18-C-6, Toluene, Tracer level Cs, 0.5 <u>M</u> HNO_3	13	Strip with high acid. For same experimental conditions, DC21C7 $D_{Cs}=4$; DC18C6 $D_{Cs}=1.5$. Toluene has low flash point.
Dietz and Horwitz (1990)	0.33 <u>M</u> di-tert-butylbenzo-24-C-8, 1-octanol, 3.0 <u>M</u> HNO_3	10	Decreasing [CE] with time, indicating that solubility limits were exceeded. Equilibrium CE concentration of 0.14 <u>M</u> translated to $D_{Cs} \sim 2.5$. With MIBK as solvent, under same conditions, $D_{Cs} = 15$. MIBK not a desirable solvent. Flat extraction curve at stripping end suggests inefficient stripping; 0.1 <u>M</u> H_2SO_4 will strip.

Table A.1. (contd)

Literature Source	Experimental Conditions	$D_{Cs}^{(a)}$	Comments
Lumetta et al. (1993)	0.05 <u>M</u> HDNNS, 0.05 <u>M</u> di-tert-butylbenzo-21-C-7, toluene, 1.0 <u>M</u> HNO ₃	~ 14	Significant sodium interference at 1 to 4 <u>M</u> NaNO ₃ . Toluene has low flash point. With octanol rather than toluene under same conditions $D_{Cs} = 0.3$.

(a) Cesium distribution coefficient: $[Cs]_{\text{organic}}/[Cs]_{\text{aqueous}}$ at equilibrium for 1 batch contact.

Table A.2. Solvent Extraction: Cobalt Dicarbolides

Literature Source	Experimental Conditions	$D_{Cs}^{(a)}$	Comments
J. Rais et al. (1976)	0.01 <u>M</u> cobalt dicarbolid, nitrobenzene, 0.5 <u>M</u> HNO_3	22	Higher D_{Cs} at lower acidity. Other solvents, such as CCl_4 , C_6H_6 , had low dicarbolid solubilities, and low D_{Cs} . Good dicarbolid solubility in TBP.
Scasnar and Koprda (1978)	0.01 <u>M</u> cobalt dicarbolid, nitrobenzene, 1.0 <u>M</u> HNO_3	11.8	Higher D_{Cs} at lower acidity. Greater selectivity for Zr at higher acidity. Zirconium, ruthenium extracted somewhat; zinc, cobalt, cesium not extracted.
Scasnar and Koprda (1979)	0.01 <u>M</u> cobalt dicarbolid, nitrobenzene, 1.0 <u>M</u> HNO_3	8.1	Cesium separation from zirconium better as compared to Cu ferrocyanide, Co ferrocyanide, and ammonium molybdophosphate ion exchangers under same experimental conditions.
Koprda and Scasnar (1979)	0.01 <u>M</u> chlorinated cobalt dicarbolid, nitrobenzene, 2.5×10^{-4} <u>M</u> $CsNO_3$, 0.05 <u>M</u> HNO_3	21.5	$D_{Cs} > D_K > D_{Na} > D_{Ru,Rh} > D_{Zr,Nb}$. All D values decrease with increasing HNO_3 . Selectivity for Cs increases with increasing HNO_3 . As increases, Cs extraction decreases. Chlorinated dicarbolid may give more stable Cs-dicarbolid complex; however, degradation may release Cl^- leading to corrosion of equipment.

Table A.2. (contd)

Literature Source	Experimental Conditions	$D_{Cs}^{(a)}$	Comments
Scasnar and Koprda (1980)	0.01 <u>M</u> cobalt dicarbolyde, nitrobenzene, 1.0 <u>M</u> HNO_3	11.7	D_{Cs} increases with decreasing HNO_3 . Dicarbolyde and chlorinated dicarbolyde give same extraction results.
Koprda and Scasnar (1980)	0.1 <u>M</u> cobalt dicarbolyde, nitrobenzene, 1.4 <u>M</u> HNO_3	22.4	Studied extraction of cesium from milk.
Koprda et al. (1983)	0.1 <u>M</u> cobalt dicarbolyde, nitrobenzene, 0.5 <u>M</u> HNO_3	24.6	Studied extraction from lung, liver tissue, milk, and urine (value given is from lung tissue in 0.5 <u>M</u> HNO_3).
Romanovskii et al. (1992)	0.097 <u>M</u> chlorinated cobalt dicarbolyde, nitrobenzene, 0.01 <u>M</u> Cesium, 1.0 <u>M</u> HNO_3 .	116.9	D_{Cs} decreased with increasing acid, and decreased significantly as cesium concentration reached 0.1 <u>M</u> .

(a) Cesium distribution coefficient: $[Cs]_{organic}/[Cs]_{aqueous}$ at equilibrium for 1 batch contact.

Table A.3. Precipitation: Alum

Literature Source	Experimental Conditions	D _F	Comments
Rupp (1955)	Potassium alum, Ammonium alum, 80-90°C, pH < 2.5.	> 99	Method used to produce cesium for commercial uses. Removal of ruthenium, rare earths, and alkaline earths preceded cesium precipitation. Sulfate in alum undesirable in glass.

Table A.4. Precipitation: Ferro- and Ferricyanides

Literature Source	Experimental Conditions	D _F	Comments
Barton et al. (1958)	0.001 <u>M</u> Nickel ferrocyanide, 10 ⁻⁴ <u>M</u> Cesium, 0.1 <u>M</u> Urea, 2.5 <u>M</u> HNO ₃	33	Tested other ferrocyanides, e.g., Fe(III), Cu(II), Zn, Uranyl, and ferricyanides, e.g. Ni, Fe(III), Cu(II), Uranyl. Ni ferrocyanide gave highest cesium recovery and smallest volume of precipitate formed. HNO ₃ concentrations from 0.1 to 3 <u>M</u> had little effect on precipitation. HNO ₃ concentrations > 10 <u>M</u> resulted in oxidation of ferro to ferricyanide. Interferences include iron, uranium. 0.4 <u>M</u> Sodium nitrate had little effect on cesium precipitation.
Van Tuyl and Moore (1959)	0.001 Nickel ferrocyanide, 10 ⁻⁴ <u>M</u> Cesium, 0.1 <u>M</u> Urea, 2.2 <u>M</u> HNO ₃	33	Other ferro- and ferricyanides tested. At least 0.00075 <u>M</u> Ni ferrocyanide required to achieve >90% cesium recovery. Ni-ferrocyanide gave best results in recovering Cs from full level unconcentrated waste (HAW), using 0.005 <u>M</u> Ni-ferrocyanide, and 5 minute - 5 hour contact time; D _F =333. No apparent radiolytic degradation. Addition of ammonium ion increased cesium recovery by Ni ferrocyanide.

Table A.5. Precipitation: Phosphotungstic Acid

Literature Source	Experimental Conditions	D _F	Comments
Beard and Schmidt (1964)	0.017 <u>M</u> PTA, 0.017 <u>M</u> Cs, 0.86 <u>M</u> HNO ₃	50	Plant-scale test on Purex IWW waste to demonstrate flowsheet developed on laboratory scale. Flowsheet involved centrifugation, precipitation, centrifugation, cake wash, and cake removal steps. Decontamination factors for other isotopes not determined. Precipitation for 1 hour at 25°C.
Bray et al. (1984 unpublished)	0.001 <u>M</u> PTA, 0.001 <u>M</u> Cs, 1.0 <u>M</u> HNO ₃	36-74	Laboratory-scale test using acidified simulated West Valley waste. Value given was for 1 hour contact time at 25°C; Supernate from first contact recontacted with 0.001 <u>M</u> PTA, overall D _F > 10 ⁴ . Higher D _F at 15 minutes, 25°C, and high acid concentrations. At 60°C, 2.5 minutes required for each contact. Resulting precipitate 10-50 microns in diameter. Water washing decreased particle sizes by ~33X.

Table A.5. (contd)

Literature Source	Experimental Conditions	D_F	Comments
Lumetta et al. (1993)	3×10^{-4} M Sodium Phosphotungstate, 7×10^{-4} M Cs, 1.1 M HNO_3	88.7	Tests done on synthetic CC wastes. 16 hour contact times. Second addition of same amount of sodium phosphotungstate to solution and 16 h stirring, overall $D_F = 1300$.
Grossi et al. (1992)	4.3×10^{-4} M PTA 1.5×10^{-4} M Cs, 1.1 M HNO_3 , 25°C	137	Tests done on synthetic 1AW-MTR waste. 14 hour contact time. One batch contact. For 2.5 hour contact times, $D_F = 68.4$. At shorter contact times, D_F higher after centrifuging rather than filtering precipitate. At 50°C and 14-hour contact time for the same reactant concentrations, $D_F = 39$.

Table A.6. Ion Exchange: Ferrocyanides

Literature Source	Experimental Conditions	Cesium Separation/Capacity	Comments
<u>Molybdenum Ferrocyanide</u> Baetslé et al. (1965)	0.1M H ⁺	H ⁺ [M] 0.001 0.01 K Cs ⁺ /H ⁺ 80 27 K Rb ⁺ /H ⁺ 39 10 K K ⁺ /H ⁺ 18 8 K Na ⁺ /H ⁺ 2.3 1.8	Greater selectivity higher capacity at higher [H ⁺]. Gradually dissolves in 2M HNO ₃ . Attacked even at 0.5M HNO ₃ . Can be eluted only 3 times with 4M NH ₄ NO ₃ . Selectivity diminishes with increased [ion]. Superior to ZrP. Fast kinetics.
Baetslé et al. (1973)	2M HNO ₃ , 0.07M Al, 0.1M Fe, 0.5M Na, 0.04M Mg, 0.02M Ni, 0.5g/L Cs	D _F = 10 ⁴ λ _d dropped from 66 to 45 after 6 load/elute cycles	Elute with 5M NH ₄ NO ₃ and 0.1M HNO ₃ . Presence of Ni gives rise to acid insoluble deposits in pores. Approximately 35 mg/g remains after dilution.
Szlaurová et al. (1979)	2M HNO ₃ , Traces of Sc, Zr, Nb, Cs, Ce, Eu	~ 100% Cs removal	Also removed 96% of Ce, 43% of Zr, 63% of Nb.
Suss and Pfrepper (1981)	≤ 3M HNO ₃ , 0.3M Ce, 1M Na, 0.08M Zr, 0.06M Mo, 0.05M Cs, 0.03M Ba	K _d = 5000 mL/g only @ 1M HNO ₃	Fairly fast kinetics. Loses capacity at > 1M H ⁺ . Affected by competing ions (K _d 30% less).

Table A.6. (contd)

Literature Source	Experimental Conditions	Cesium Separation/Capacity	Comments
<u>Molybdenum Ferrocyanide (contd)</u> Loewenschuss (1982)	Conditions not given	35 mg/g capacity	Irreversibly takes up cesium. Cannot be eluted in acid if Ni present in waste.
<u>Tungsten Ferrocyanide</u> Baetslé et al. (1965)	0.1M H ⁺	Experimental data not given	Chemical stability in acid > FeMo but half the capacity of FeMo. Same capacity as ZrP. Slow kinetics.
<u>Titanium Ferrocyanide</u> Krylov et al. (1988)	1.0M HNO ₃ , no other cations	D _F =20 0.05g/L Cs D _F =6 1.0g/L Cs	Adsorption of Cs decreases with Na > Ni > Al > Rb.
<u>Zinc Ferrocyanide (II & III)</u> Loewenschuss (1982)	Non-acid solution	K K ⁺ /Cs ⁺ = 78 307 mg/g capacity	In strong acid, iron oxidizes.
Filippov et al. (1992)	3M HNO ₃ , 0.18M Fe, 0.05M Ca, 0.015M Cs, trace Ni, Ba, Cr	7 mg/g	Acid oxidizes iron. 115 mg/g in neutralized waste 80% desorbed in 8M HNO ₃ (10CV).
<u>Zinc Hexacyanocobaltate</u> Faubel and Ali (1986)	pH=9.5 to 8M HNO ₃ , 0-3.6M Na	Retention ~25% for 2 mg/g	Used NH ₄ ⁺ instead of Zn ⁺ . Affected by Na ⁺ and H ⁺ .

Table A.6. (contd)

Literature Source	Experimental Conditions	Cesium Separation/Capacity	Comments
<u>Cadmium Ferrocyanide</u> Suss and Pfrepper (1981)	$\leq 3\text{M}$ HNO_3 , 0.3M Ce, 1M Na, 0.08M Zr, 0.06M Mo, 0.05M Cs, 0.03M Ba	$K_d = 5 \times 10^4$ only @ 1M HNO_3	Very fast kinetics. K_d drops by 9/10 in mixed solution compared to HNO_3 solution. Eluting Cs most difficult part.
<u>Nickel Ferrocyanide</u> Suss and Pfrepper (1981)	$\leq 3\text{M}$ HNO_3 , 0.3M Ce, 1M Na, 0.08M Zr, 0.06M Mo, 0.05M Cs, 0.03M Ba	$K_d = 10^5$ @ 1M HNO_3 only	Loses 70% of K_d with competing ions.
Loewenschuss (1982)	Review article		In a comparison of Ni, Co, Zn, Ag, U, and Cd, ferrocyanides, Ni has highest distribution coefficient for Cs.
Faubel and Ali (1986)	pH=7 to 8M HNO_3	20 mg/g 95% @ 1M HNO_3	Slow kinetics.
Jacobi and Streat (1990)	1M NaNO_3	160-170 mg Cs/g $\lambda_d = 220-300$	Without acid, thus not applicable.
Lumetta et al. (1993)	1.0M HNO_3 , 4.7M Na^+ trace Al, Fe, B, K 0.0006M Cs^+	$\lambda_d = 1$ $K_d = 72 \text{ mL/g w/ Na}^+$ $K_d = 240 \text{ mL/g w/o Na}^+$	On Amberlite support. Na^+ greatly affects Cs removal.

Table A.6. (contd)

Literature Source	Experimental Conditions	Cesium Separation/Capacity	Comments
<u>Nickel Ferrocyanide (contd)</u> Filippov et al. (1992)	3M HNO ₃ , 0.18M Fe, 0.05M Ca, 0.015M Cs, trace Ni, Ba, Cr	3 mg/g	Acid oxidizes iron. 30 mg/g in neutralized waste. With 8M HNO ₃ , only 40% eluted in 10 CV.
<u>Cobalt Ferrocyanide</u> Scasnar and Koprda (1979)	1.0M HNO ₃ , Radioactive Ce, Ru, Zr, Zn, Co, and Cs	approximately 100%	High efficiency (100%), but low selectivity. 10% of Ru, 74% of Zr, 93% of Zn, 91% of Co also adsorbed.
Tanihara (1991)	3M HNO ₃ only 10 ⁻⁵ M hydrazinium 10 ⁻³ M Cs	K _d > 10 ⁸ mL/g	K _d increases from 4300 to 10 ⁸ with addition of hydrazinium. Co ferrocyanide appears to have higher K _d than Ni, Zn, Mo, and Cu ferrocyanides.
<u>Copper Ferrocyanide</u> Watari et al. (1967)	1M HNO ₃	D _F = 100 K _d = 10 ³ mL/g	On Amberlite resin. Fe oxidizes in high acid concentration (> 1M). Adsorption Ratio: Na < K < Rb < Cs at 1:10:10 ³ :10 ⁴ .
Scasnar and Koprda (1979)	1.0M HNO ₃ . Radioactive Ce, Ru, Zr, Zn, Co, and Cs	approximately 100%	High efficiency (100%), but low selectivity. 24% of Zr, 16% Zn, 33% of Co also adsorbed.

Table A.6. (contd)

Literature Source	Experimental Conditions	Cesium Separation/Capacity	Comments
<u>Copper Ferrocyanide (contd)</u>			
Lee and Streat (1983)	pH=0.35, $[\text{Na}^+] = 5$, 0.018M Fe^{3+}	$K_d = 3200 \text{ mL/g}$ 200 mg/g	Affected by Mg, Fe. Not stable in acid solution, 7%-20% weight loss. 25% of cesium desorbs @ 1M HNO_3 .
Beaven et al. (1988)	1M HNO_3	$D_F = 33$	Fast kinetics compared to TiP, ZrP. Not affected by Na^+ at 1M concentrations.
Tanihara (1991)	3M HNO_3 only 10^{-5}M hydrazinium 10^{-3}M Cs	$K_d > 10^5 \text{ mL/g}$	Usual low value improved by addition of 10^{-5}M hydra- zinium (K_d from 100 to 200). Prevents $\text{K}_2\text{Cu}_3\text{FC}$ oxidation. 10^{-4}M amidosulfate prevents oxidation.
Filippov et al. (1992)	3M HNO_3 , 0.18M Fe, 0.05M Ca, 0.015M Cs, trace Ni, Ba, Cr	$D_F = 50$ 5 mg/g	Acid oxidizes iron. Capacity 100 mg/g in neutralized waste. Better performance than Zn, Ni ferrocyanides (easier to elute, more stable).

Table A.7. Ion Exchange: Phosphates

Literature Source	Experimental Conditions	Cesium Separation/ Capacity	Comments
<u>Ammonium Molybdophosphate</u> Smit and Jacobs (1966)	3M HNO ₃ , 0.5M Fe, 0.9M Al, 0.04M Cr, 0.01MM Zr, 0.007M Cs	$\lambda_d = 100$	AMP-asbestos column not as effective as AMP alone. Elution required 8M ammonium nitrate or 3M ammonium nitrate plus concentrated nitric acid.
Dolezal et al. (1974)	N/A	N/A	Developed AMP on silica gel system. Studied at neutral solution.
Scasnar and Koprda (1979)	1.0M HNO ₃ Radioactive Ce, Ru, Zr, Zn, Co, and Cs	approx. 100%	High efficiency but low selectivity: absorbs 39% of Zr and 10% Ru.
Suss and Pfrepper (1981)	$\leq 3M$ HNO ₃ , 0.3M Ce, 1M Na, 0.08M Zr, 0.06M Mo, 0.05M Cs, 0.03M Ba	$K_d = 10^5$ mL/g @ 1M HNO ₃	Very fast kinetics. Resin of choice among many evaluated. Eluted only 80% of Cs after 56 CV 7.9M NH ₄ NO ₃ . Similar K_d for 3.1M HNO ₃ with and without competing ions.
Pietrelli et al. (1986)	1.1M HNO ₃ , 1M Al, 0.01M Fe, 0.006M Hg, 0.00013M Cs	$K_d = 5.5 \times 10^4$ mL/g 1048 mg/g capacity	Batch tests.
Faubel and Ali (1986)	pH=9.5 to >8 HNO ₃ , 0-3.6M Na, 0.04M Ca, 0.002M Cu & Zn, 0.007M Fe, 0.03M Mg, 0.0036 g/L Cs	D.F.[? D _F] > 100 at 60 mg Cs/g	Rapidly attains equilibrium. Success requires microcrystalline structure, but consequent hotspots prevent use in columns. Fast kinetics.

Table A.7. (contd)

Literature Source	Experimental Conditions	Cesium Separation/ Capacity	Comments
<u>Ammonium Molybdophosphate (contd)</u>			
Cunha and Sakai (1989)	pH = 1.0	120 mg/g capacity $K_d = 170$ mL/g	Adsorption is maximum at pH 1; retention decrease with $> <$ pH. Eluted with $3M$ NH_4NO_3 / $1M$ HNO_3 or $5M$ NH_4NO_3 .
Faubel and Ali (1989)	$2M$ H^+ Na, small amount of Fe, Cr, Ca	$D_F = 100,000$	Modified suspended-bed column "micro-crystalline AMP lying loosely on porous substrate."
Sebesta and Stefula (1990)	$0.1M$ HCl, $10^{-2}M$ Cs^+ , (uses PAN support)	30 mg/g capacity	PAN support slows the kinetics vs AMP crystals alone, but no influence on capacity. Elutes 92% of Cs with $5M$ NH_4^+ in 10 CV.
Kolarik (1991)	Review article	N/A	Because acid insensitive, it is difficult to elute (impossible with HNO_3). Requires NH_4NO_3 (concentrated). NaOH destroys the sorbent.
Min and Zhaoxiang (1992)	AMP + TiP, $1M$ HNO_3 , $0.1M$ Na, $0.005M$ Cs, $0.03M$ Fe, $0.02M$ Zr	62 mg/g capacity $\lambda_d = 85$	Mixture solved granulation problem. Claim exchange is better with both. Not affected by acidity at $0.5M$ to $4M$ HNO_3 . D_F affected by Na/Cs ratio. D_F for Cs: Ru=106, Zr=2300, Na=1164, Rb=1.5.

Table A.7. (contd)

Literature Source	Experimental Conditions	Cesium Separation/ Capacity	Comments
<u>Ammonium Phosphotungstate - Zirconium Phosphate Mix</u> Pietrelli et al. (1986)	1.1M HNO ₃ , 1M Al, 0.01M Fe, 0.006M Hg, 0.00013M Cs	K _d =515 mL/g 10 mg/g capacity	Batch tests.
Kolarik (1991)	Review article	N/A	Easier elution than ammonium molybdate counterpart and better mechanical properties. Less selective and effective than molybdate.
<u>Zirconium Phosphate</u> Baetslé et al. (1965)	1M HNO ₃ , 0.11M Fe, 0.02M Ni, 0.02M Cr, 0.07M Al, 0.6M Na, 0.6M Mg	D _F =100 9.6 CV @ 100% 5.8 mg/g capacity	Loses 25% capacity with 2M HNO ₃ eluent. NH ₄ ⁺ , Rb ⁺ , and rare earths interfere. Selective for Cs at low concentrations. Should not be used at >0.5M HNO ₃ (fixation too weak).
Suss and Pfrepper (1981)	≤3M HNO ₃ , 0.3M Ce, 1M Na, 0.08M Zr, 0.06M Mo, 0.05M Cs, 0.03M Ba	K _d =158 mL/g @1M HNO ₃ only	50% loss of K _d with completing ions.
Pietrelli et al. (1986)	1.1M H ⁺ , Al, Fe, Hg	K _d =10.4 mL/g 26 mg/g capacity	Poorly effective as compared to PAA, AMP.
Faubel and Ali (1986)	pH=7 to 8M HNO ₃	3 mg/g to 100 mg/g	Ineffective in >0.1M HNO ₃ or 3.6M NaNO ₃ . Slow kinetics.

Table A.7. (contd)

Literature Source	Experimental Conditions	Cesium Separation/ Capacity	Comments
<u>Zirconium Phosphate (contd)</u>			
Beaven et al. (1988)	1M HNO ₃	D _F =20	Adversely affected by Na ⁺ at 1MH ⁺ ; D _F drops to 3.
Min and Zhaoxiang (1992)	N/A	N/A	Exchanger "block[s] up the exchange column due to released microamounts of phosphate groups combined with trivalent action in the feed solution."
<u>Titanium Phosphate</u>			
Jones (1966)	2M HNO ₃ , 2M Na, 0.03M Al, 0.067M Fe, Ni, 0.01M Cr (PAW), 10 ⁻³ M Cs	19.8 mg/g in acid 92.4 mg/g in water	With 1.0M HNO ₃ , K _d =556 mL/g, and 0.27 mg/g capacity, no competing ions. 554 to 460 drop in K _d with 0.5 to 1.5M increase in acid concentration. 85% eluted with 5M NH ₄ NO ₃ .
Baetslé et al. (1973)	2M HNO ₃ , 0.07M Al, 0.1M Fe, 0.5M Na, 0.04M Mg, 0.02M Ni, 0.5g/L Cs	λ _d =53-49	Better stability than FeMo with multiple elution cycles, but less separation potential. Eluted effectively with 4M NH ₄ NO ₃ and 0.1M HNO ₃ .
Suss and Pfrepper (1981)	≤3M HNO ₃ , 0.3M Ce, 1M Na, 0.08M Zr, 0.06M Mo, 0.05M Cs, and 0.03M Ba	1M HNO ₃ only, no competing ions K _d =300 mL/g	30% drop in K _d with competing ions.

Table A.7. (contd)

Literature Source	Experimental Conditions	Cesium Separation/ Capacity	Comments
<u>Titanium Phosphate</u>			
Faubel and Ali (1986)	pH=7 to 8M HNO ₃	65% cesium removal at 1M HNO ₃ Capacity: 15g Cs/kg	Affected by 3M Na ⁺ .
Beaven et al. (1988)	1M HNO ₃	D _F =16	Appears to be strongly affected by Na ⁺ . D _F = 4 at 1M Na ⁺ .
Min and Zhaoxiang (1992)	N/A	N/A	Exchanger "block[s] up the exchange column due to released microamounts of phosphate groups combined with trivalent action in the feed solution."
<u>Tin Phosphate</u>			
Jones (1966)	2M HNO ₃ , 2M Na, 0.03M Al, 0.067M Fe, Ni, 0.01M Cr (PAW) 10 ⁻³ M Cs	0.8 mg/g vs. 26 mg/g in water	Low selectivity versus TiP. 357 to 15 drop in K _d with 0.5 to 1.5M increase in acid concentration.

Table A.8. Ion Exchange: Oxides

Literature Source	Experimental Conditions	Cesium Separation/Capacity	Comments
<u>Manganese Dioxide</u> Beaven et al. 1988	1M HNO ₃ , 1M Na	D _F =1.33 D _F =1.37	Not effective for cesium removal.
<u>Titanium Oxide</u> Beaven et al. 1988	pH=2	8% cesium removal	Did not function in acid (1M HNO ₃).
Faubel and Ali 1986	pH=10 to 8M HNO ₃	10% cesium removal Capacity: 5 mg/g @1M HNO ₃	Strongly affected by Na ⁺ ion.
<u>Antimony Pentoxide</u> Faubel and Ali 1986	pH=10 to 8M HNO ₃ , 10 ⁻³ M Cs ⁺	Capacity: 15 mg/g, 100% Cs removal @ 1M HNO ₃ , Drops off strongly when 3.6M Na ⁺ added	Less affected by Na ⁺ than titanium oxide, cobalt ferrocyanide exchangers. <u>Slow</u> kinetics.

Table A.9. Ion Exchange: Others

Literature Source	Experimental Conditions	Cesium Separation/Capacity	Comments
<u>Polyantimonic Acid</u> Pietrelli et al. 1986	1.1M H ⁺ Al, Fe, Mg	K _d =61 mL/g 1.18 mg/g capacity	Removes Sr and Cs.
Beaven et al. 1988	Removes Sr and Cs. 1M HNO ₃	D _F =11 after 24 hrs D _F =5 after 5 hrs	Strongly affected by 1M Na ⁺ ; D _F = 1.2. Slow kinetics.
<u>Macrocyclic Superligands</u> Lumetta et al. 1993	1.0M HNO ₃	λ _d = 2.5	Low Cs capacity.
Camaioni et al. 1992	5M HNO ₃ , 3M Na, trace others	N/A	Chromatographic separation rather than ion exchange. Required 3 X loading volume to elute.
<u>Crystalline-Silico Titanates</u> Bray 1993	1 M nitric acid	K _d ≈ 3000 g/ml	Powder form only. Pellet forms under development.

Table 9. (contd)

Literature Source	Experimental Conditions	Cesium Separation/Capacity	Comments
<u>Zeolites</u>			
Nelson et al. 1964	Clinoptilolites $[H^+] = 0.45$, $[Na^+] = 0.60$, $[Fe^{2+}] = 0.17$, $[Al^{3+}] = 0.08$, $[Cs^+] = 10^{-3}$	$\lambda_d = 80$	Best eluted with 75% $(NH_4)_2CO_3$ and 25% NH_4OH ; required 8CV. Acid dissolved the zeolite, 2% per cycle during 7 cycles.
Murphy and Buckingham 1978	$[H^+] = 1.0$, 0.2M Al, 0.002M Ca, 0.002M Cs, 0.2M Fe, 0.7M Na	$K_d = 43$ zeolon-900 $K_d = 4.3$ ARC-359 $K_d = 6.5$ AW-500	High Al, Fe, Na D_F . No tests on dissolution. Tested at 1.01M H^+ .
Suss and Pfrepper 1981	clinoptilolites) < 3M HNO_3 , 0.3M Ce, 1M Na, 0.08M Zr, 0.06M Mo, 0.05M Cs, 0.03M Ba	$K_d = 158$ mL/g @ 1M HNO_3 only	Very slow to reach equilibrium (960 min). Solution in acid media affected by competing ions.
Turner et al. 1985	wide range of pH	not given	IE-96 and Zeolon 500 have high K_d for pH 3 to 12. Zeolites sensitive to $[Na^+]$. ZrP and AMP preferred at pH < 3.
Mimura et al. 1992	ferrerites 1M HNO_3 0.01M Cs^+	$\lambda_d = 40$	"Ferrierites have higher selectivity for Cs than other zeolites." Strongly affected by H^+ and Rb^+ , also affected by K^+ and Na^+ . 1M HNO_3 (85%) and 1M KNO_3 (100%) elutes column.

Table A.10. Ion Exchange: Summary Of Exchanger Properties

Exchange Material	Kinetics	Capacity (mg/g)	K _d (mL/g)	D _F	Elute	Solubility in Acid	Selectivity (decrease due to added ions)
FERROCYANIDES						Oxidizes Fe in H ⁺ Dissolves in 0.5M	
Molybdenum	Fast	35	5x10 ³	10 ⁴	Difficult w/ Ni		↓ 30%
Tungstate	Slow	15	--	--	--	Fairly Insoluble	--
Zinc	--	23-32	3.5x10 ³	--	80% w/ 8M HNO ₃	--	↓ 75%
Titanium	--	--	--	20	--	--	Affected by Na
Cadmium	Fast	--	5x10 ⁴	--	Difficult	--	↓ 90%
Nickel	Slow	20	240	20	--	--	70% strongly affected by Na
Cobalt (+ hydrazinium)	--	--	4x10 ³ 10 ⁸	>100	--	--	Strongly affected by Zr, Zn, Co
Copper (+ hydrazinium)	Fast	200 @ pH = 0.3; 5 @ [H] = 3	10 ³ 10 ⁵	33-100	Easy	25% loss in 1M H ⁺	--
PHOSPHATES							
Ammonium Phosphomolybdate	Very Fast	60	10 ⁵	10 ⁵	Difficult Req. 5M NH ⁺	Fairly Insoluble	Affected by Rb, Ru, Zr
Ammonium Phosphotungstate	--	10	500	--	Easier than AMP	--	Worse than AMP
Zirconium Phosphate	Slow	3-26	10-158	20	--	Dissolves in 0.5M	50% affected by NH ₄ , Rb

Table A.10. (contd)

Exchange Material	Kinetics	Capacity (mg/g)	K _d (mL/g)	D _F	Elute	Solubility in Acid	Selectivity (decrease due to added ions)
Titanium Phosphate	--	20	300	16	Easily	--	70% strongly affected by Na
Tin Phosphate	--	0.8	15	--	--	--	Less than TiP
OXIDES							
Manganese	--	--	--	1.3	--	--	--
Titanium	--	5	--	1.1	--	--	Strongly Affected by Na
Antimony	Very Slow	15 (mg/g)	-- (mL/g)	--	--	--	Strongly Affected by Na (decrease due to ion addition)
MISCELLANEOUS							
Polyantimonic Acid	Slow	1.1	61	10	--	--	Strongly Affected by Na
Macrocyclic Ligands	--	--	--	--	Requires large volume to elute	--	Chromatographic
Crystalline-Silico Titanates	unknown	--	≈ > 3000 at pH < 6	Not determined	unknown	low	high
Zeolites	Very Slow	--	4.3 to 158	--	Elute with 8CV NH ₄ CO ₃ or KNO ₃	Dissolves in acid	Strongly Affected by Na

Table A.11. Other Cesium Separation Methods: Supported Liquid Membranes, Electrochemical Ion Exchange, Electrodialysis

Literature Source	Experimental Conditions	D_F	Comments
<u>Supported Liquid Membranes</u>			
Ramadan and Danesi (1988)	3×10^{-3} M Dicyclohexyl 18-C-6 + 0.2 M HDNNS in dodecane on a Celgard® solid support, 0.2 M HNO_3	0.18	Under same conditions strontium $D_F=100$.
<u>Electrochemical Ion Exchange</u>			
Turner et al. (1987)	Zirconium phosphate ion exchange, pH=9-10	60	Selectivity over sodium = 21; Ammonium phosphotungstate unstable.
<u>Electrodialysis</u>			
Gurskii and Moskvina (1986)	Ammonium phosphomolybdate based membrane, 0.5 M CsOH + 0.5 M NaOH.	1.4 ^(a)	$\alpha_{\text{Cs/Na}} = 1.0$ to 1.9 for different membranes.

(a) Separation coefficient for cesium and sodium, $\alpha_{\text{Cs/Na}}$.

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