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Pretreatment/Radionuclide Separations of Cs/Tc from Supernates

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PRETREATMENT/RADIONUCLIDE SEPARATIONS OF CS/TC FROM SUPERNATES

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ABSTRACT

Significant improvements have been made in ion exchange and solvent extraction materials and processes available for separation of the radionuclides cesium and technetium from both acid and alkaline waste solutions. New ion exchange materials and solvent extraction reagents are more selective for Cs over sodium and potassium than previous materials. The higher selectivity gives higher Cs capacity and improved separation processes. Technetium removal has been improved by new ion exchange resins, which have either improved capacity or easier elution. Several different crown ethers have been shown to extract pertechnetate ion selectively over other anions. Organic complexants in some waste solutions reduce pertechnetate ion and stabilize the reduced species. Selective oxidation allows conversion to pertechnetate without oxidation of the organic complexants.

I. INTRODUCTION

The Department of Energy (DOE) has five sites where large volumes of high level radioactive waste (HLW) are stored in large underground tanks. The wastes at four sites are alkaline while the waste at the fifth site is acidic. The alkaline wastes have three components: insoluble solids or sludge, liquid supernates, and salt cakes. The salt cakes are soluble salts, which crystallized after evaporation of supernatant solutions. The salt cakes must be re-dissolved prior to treatment. The DOE is in the process of converting these wastes into vitrified HLW for disposal in a repository and either grouted or vitrified low level waste (LLW) forms for on-site disposal. Salt cake and supernate contain the fission products, cesium and technetium at concentrations above regulatory limits for disposal as LLW. Consequently, all sites plan to remove Cs and one site must remove Tc from salt cake and supernate solutions prior to conversion to the LLW waste form.

The Office of Science and Technology (OST) of the Environmental Management program at DOE has funded research and development (R&D) over the past seven years, which has resulted in new or improved ion exchange materials and solvent extraction reagents for removal of these radionuclides. In addition, OST has funded R&D to evaluate technologies developed in Great Britain, the Czech Republic, and Russia for application to DOE HLW supernate treatment. This paper summarizes the new technologies being developed for application to DOE HLW pretreatment.

II. CESIUM SEPARATION

A. Past Cesium Separations and Materials

Cesium separation from various solutions has been done for many years principally using ion exchange, solvent extraction, or precipitation processes. Commercial reactors use various natural and synthetic zeolites or cation exchange resins to remove Cs from contaminated water. The British use the natural zeolite, clinoptilolite, to remove Cs from wastewater prior to disposal. Zeolites and cation exchange resins have been used for Cs removal from reactor cooling basin water at DOE sites. West Valley used a titania-coated zeolite for removal of Cs from their tank waste. Prout and co-workers showed that $K_2CoFe(CN)_6$ was a highly selective ion exchange material with high capacity for Cs.[1] However, the metal hexacyanoferrates are not stable at the very high pH of present supernates at Hanford and Savannah River. The Hanford site removed Cs from alkaline supernates ($pH < 12$) by addition of metal hexacyanoferrates into the waste tanks. The hexacyanoferrates decomposed when the pH in the tanks was increased releasing the Cs back into solution. Later, Cs was recovered from supernates by cation exchange with the commercial resin, CS-100, a polymer of phenol and formaldehyde. The resin was somewhat selective for Cs over Na, but multiple adsorptions and elutions were required to obtain the desired purity. Bibler and Wallace developed a more selective resin during the mid-80's.[2] The resin was made by condensation of resorcinol with formaldehyde (RF). Precipitation of Cs with tetraphenylborate (TPB) was developed for large-scale Cs removal at the Savannah River Site (SRS) in the early 1980s. Although the process showed excellent decontamination (>40,000), decomposition of TPB catalyzed by noble metal fission products led to suspension of work on the process early in 1998. Extensive evaluation of other processes is under way to select a replacement process for TPB precipitation.

Solvent extraction of Cs has been reported using large hydrophobic organic anions such as picrate or tetraphenyl borate in an organic solvent such as chloroform or toluene.[3] Neutral extractants such as trioctylphosphine oxide and tributyl phosphate and hydrophobic organic acids such as di-2-ethylhexylphosphoric acid, alkyl carboxylic acids and 4-sec-butyl-2-(α-methylbenzyl)phenol have been used to extract Cs.[3]

The French, Russians and Czechs have developed ion exchange and solvent extraction materials and processes for acid solutions because their HLW is stored as acid solutions. Acid waste solutions typically do not have as high a concentration of the competing ions, sodium and potassium, as the alkaline wastes. However, resins such as CS-100 and RF do not absorb Cs from acid solutions. Ammonium molybdophosphate (AMP) and zirconium phosphate have been used for many years to remove Cs from acid solutions primarily in analytical applications. The small particle size of these materials made large-scale application difficult. The metal hexacyanoferrates have also been used where the acid concentration was not high enough to oxidize the ferrous ion to ferric ion.

B. Recent Developments in Ion Exchange

Recent R&D in Cs ion exchange has been funded by the Efficient Separations and Processing Crosscutting Program and the High Level Waste Tanks Focus Area of OST. The work has resulted in several materials with improved properties for removal of Cs from supernates. New materials include crystalline silicotitanate (CST), SuperLig^{tm}644, AMP incorporated in a polyacrylonitrile support (AMP-PAN), Diphonix-CS, inorganic supports for AMP and other small particle size ion exchange materials, and metal hexacyanoferrates such as KCoFC. Table 1 summarizes the materials developed and tested for use with DOE supernates.

Table 1

Material	Exchange Site	Support	pH Range for Use	Column Flow Rate, BV/hour	Elutable
AMP-PAN	Inorganic	Organic	0-10	20-100	Possibly
CST	Inorganic	Inorganic	0-14	6-12	No
Diphonix-CS	Organic	Organic	10-14	Not determined	Yes
Hexacyanoferrates	Inorganic	Inorganic & Organic	0-12	6-20	Yes
SuperLig^{tm} 644	Organic	Organic	10-14	3-6	Yes

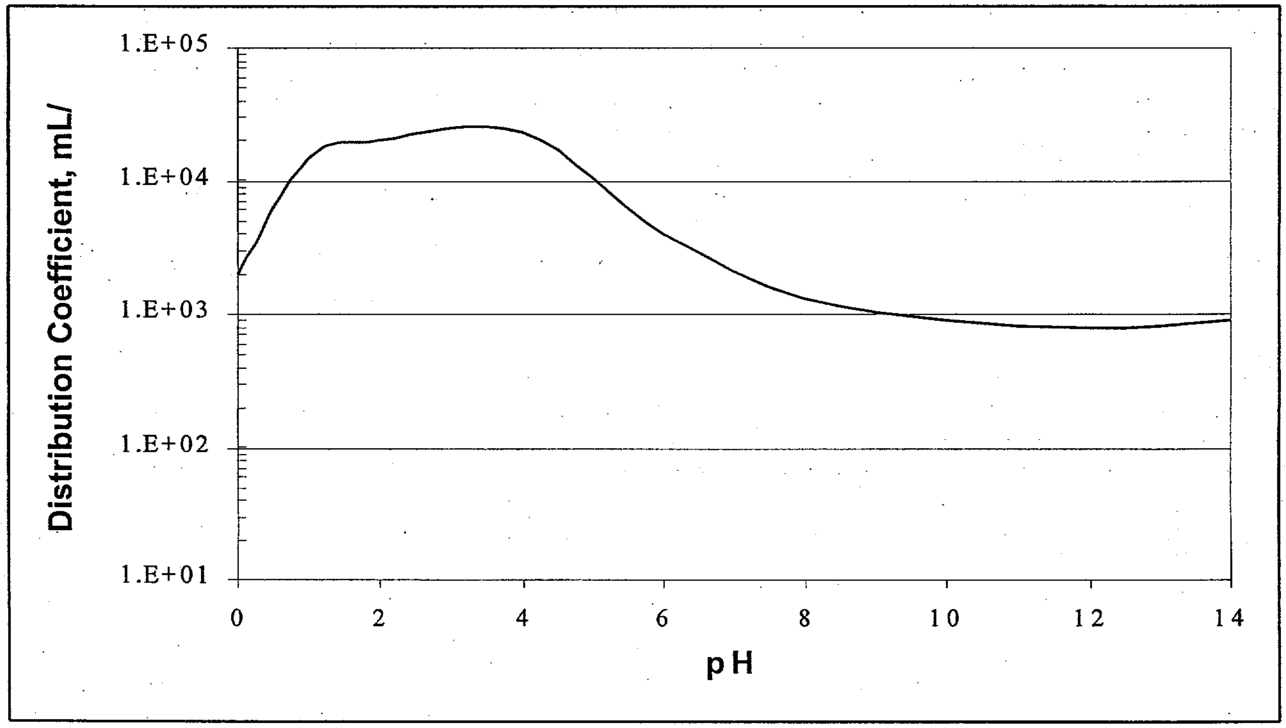
Sebesta and co-workers have shown that polyacrylonitrile (PAN) can be a support for inorganic ion exchange materials with small particle size.[4] They have made and tested composite absorbers with AMP. The resulting resin is readily usable in laboratory or plant columns for Cs removal. These composite absorbers have been shown to work at flow rates up to 100 column volumes (CV) per hour, indicating rapid exchange kinetics. The material shows good selectivity and high capacity for Cs in acid solutions. Performance in alkaline solutions is limited with decomposition occurring at pH of >10. AMP-PAN was tested with actual acid waste at INEEL.[5,6] Fifty- percent breakthrough was observed at 1400 CV. Elution of Cs from

AMP-PAN with 8 M HNO_3 was reported by INEEL,[6] although other workers have reported that AMP decomposed during attempts to elute.[4]

Work on CST started in February of 1992 and material was commercially available by 1995. Two forms of CST are now available; powder (UOP IONSIV^{tm} IE-910) and engineered (UOP IONSIV^{tm} IE-911). CST selectivity for Cs is based on controlling the largest lattice spacing in the material to less than 0.8 nm.[7] The small spacing allows the Cs ion to enter, but excludes the larger hydrated Na ion. CST Consequently, the selectivity of Cs over Na is very good and selectivity of Cs over K is also good. Extensive studies have been done to elucidate the properties of the material and to develop models for use.[7-16]

CST has a wide range of applicability from acid to highly alkaline solutions. Figure 1 shows the distribution coefficient of Cs as a function of pH for a simulated waste solution with total Na concentration of 5.7 M.[7] As a result of the strong adsorption of Cs on CST, all attempts to elute Cs have been unsuccessful. Maximum Cs adsorption is obtained in the pH range of 2-6. Small laboratory tests of CST have been done with wastes at Hanford, Idaho (INEEL), Oak Ridge (ORNL), and Savannah River.[6,7,17-21] CST showed the highest Cs distribution coefficients in batch testing and showed 50 % breakthrough at more column volumes than RF or Superlig resins.[7] A full-scale demonstration was conducted at ORNL where 25,000 gallons of alkaline waste supernate was treated to remove ^{137}Cs.[7] The Cs-loaded CST passed Toxic Characteristic Leach Protocol (TCLP) tests, which allow the material to be disposed as LLW at the Nevada Test Site. Work has also demonstrated that CST can be vitrified along with sludge to make a HLW glass with leach characteristics, which meet or exceed the requirements for disposal in a repository.[22] The material also adsorbs Sr and actinides which can be advantageous for some high level waste supernatant solutions such as those at Savannah River.

Figure 1: Cs Distribution Coefficient with Change in pH



Diphonix^{tm} is a geminal diphosphonic acid resin, which is chemically bonded to a styrene-divinylbenzene support and has been shown to sorb actinides. Diphonix-CS^{tm} resin adds phenolic groups attached to the polymeric matrix to bind Cs.[23-24] Thus, Diphonix-CS^{tm} resin can be used to simultaneously adsorb actinides, Cs and Sr from high level waste solutions similar to CST, but the resin is elutable. The resin has not been tested with actual wastes yet, but has performed well with Hanford simulant.[24]

Sebesta and co-workers have also incorporated KCoFC into the polyacrylonitrile (PAN) matrix to obtain improved column operation.[4] These composite resins also demonstrate rapid kinetics of adsorption. Elution has been demonstrated by oxidation of the ferrous ion to ferric with 8 M nitric acid. The reaction is reversible so the resin can be reused until radiation damage to the organic matrix becomes so severe that resin capacity is lost. KCoFC has been incorporated into membranes using patented Web^{tm} technology at 3M Co.[25] Membranes are fabricated into filter cartridges for use in standard filter housings. The principal advantage of the membranes is high flow rates, which can be attained due to rapid kinetics from the very small particle size needed to fabricate the membrane. The membrane was successfully demonstrated with West Valley waste, which has a pH of about 10. Other studies have been done with metal hexacyanoferrates with the metal being Cu, Ni, or Zn instead of Co.[6, 26-27] A commercial KCuFC from Russia was tested at INEEL.[6] Simulant tests indicated breakthrough should occur at about 2000 CV. Tests with actual acid waste solutions showed 50 % breakthrough at 350 CV in one test and 20 % breakthrough after 800 CV in another test. This performance is worse than the AMP-PAN material for acid solutions, but the material appears to be more easily eluted and regenerated for subsequent reuse.

Lilga and coworkers are developing KNiFC thin films coated on high surface area Ni electrodes with electrochemical switching of the valence of iron to load and elute Cs.[28-29] When iron is reduced from ferric to ferrous, a cation must be taken up to maintain electrical neutrality of the film. When ferrous is oxidized to ferric, a cation must be released to maintain electrical neutrality of the film. The concept works well, but must be engineered to provide adequate capacity. Added chemicals are minimized and the eluate can be reused several times to minimize elution volumes and secondary waste volumes. The technology has worked well in neutral solutions and can be used for the acid wastes at INEEL.

SuperLig^{tm} 644 resin has high selectivity for Cs in alkaline solutions because it is based on a crown ether ligand attached to an organic substrate. The basis of selectivity is the size of the opening in the crown ether, which is sized to accept Cs and reject the larger hydrated Na ions. The crown ether also improves selectivity for Cs over K. An inherent problem with large macrocyclic ligands such as the crown ether compounds is kinetics of adsorption and elution. Consequently, columns must be operated at low flow rates with adsorption being best at 2-3 CV per hour with elution at 1 CV per hour.[18,20,30,31] All organic resins, including SuperLig^{tm} 644, suffer from changes in volume as a result of changes in ionic strength of the solutions used for loading, washing, and elution.[20] The resin is subject to loss of organic during loading presumably due to oxidation.[20] The life of the resin is uncertain because the same resin has not been reused a sufficient number of times to determine the loss of capacity due to radiation and chemical oxidation. However, studies of the stability toward radiation and oxidation for early samples of Superlig^{tm} 644 indicated that Superlig^{tm} 644 was less stable to oxidation and radiation than RF resin.[31]

The 3M Web^{tm} technology has also been used with SuperLig^{tm} 644 and RF resins. A membrane with SuperLig^{tm} 644 was tested with ORNL waste at a flow equivalent to 49 CV per hour. Breakthrough was obtained at 60 % of the value observed with a column of SuperLig^{tm} 644 at a flow rates of 3 and 6 CV per hour. Lower rates were not tested for the membrane.[20]

AEA Technologies in Great Britain has developed an electrochemical elution for elutable resins such as RF or SuperLig^{tm} 644. The technology was demonstrated with RF resin and ORNL tank waste. The elutable ion exchange resin was placed in a specially designed cell and Cs was loaded as in typical column operation. After washing to remove residual waste, hydrogen ion was produced electrochemically to elute Cs from the resin. The eluate was removed, the cell washed with water, and the resin regenerated with NaOH to prepare for the next cycle. Excellent performance was observed with minimum addition of chemicals and maximum concentration of Cs. Several loading and elution cycles were performed with the same batch of resin.[32]

RF resin was tested for comparison with many of the other materials developed for Cs. [2,18,20,30,31] Performance of RF resin was highly variable because it was discovered that the resin was subject to oxidation during storage and pretreatment. Resin which was stored under nitrogen and prepared immediately before use performed much better than resin stored in air or prepared days ahead of use and not protected from oxidation after preparation. Studies were done by Hubler to try to improve the resistance of the resin to oxidation.[33-35] He showed that during oxidation a rearrangement between hydrogen on carbon adjacent with the hydroxyl group responsible for ion exchange. Fluoride or methyl groups were used to replace the hydrogen, but the modification reduced the Cs selectivity and capacity of the resin. Properly stored and prepared, RF resin can give results comparable to SuperLig^{tm} 644, but loses capacity due to oxidation so that resin must be replaced after only 5-6 load-elute cycles.

More recent work has shown that sol gel technology can be used to make spherical inorganic exchangers as pure materials or as composites.[36,37] Initial work centered on sorbents for Sr, but the method is applicable to Cs exchangers such as AMP and zirconium phosphate. Hydrous titanium oxide and titanium monohydrogen phosphate are the inorganic support materials tested for composite exchangers. A test batch of spheres was shipped to INEEL recently for testing Cs removal from INEEL acid waste solution.[36] The materials are not commercially available at this time.

B. Recent Developments in Solvent Extraction

Rais, et. al. first used cobalt dicarbollide dissolved in nitrobenzene to extract Cs from acid solutions.[38] The process was further developed and demonstrated in Russia.[39] Recent Russian work has been supported by OST to change the process for application to acid wastes at the Idaho National Engineering and Environmental Laboratory (INEEL).[40-43] The revised process uses chlorinated cobalt dicarbollide in a fluorocarbon solvent. The process has been tested at INEEL on actual waste with excellent results. Selectivity of Cs over Na was as high as 60 and as high as 21 over K in a single batch extraction. Selectivity during stripping was even higher with any Na and K remaining in the solvent. A decontamination factor of 100 was obtained in tests with a single wash step.

There have been many studies of crown ethers and combinations of crown ethers with calixarenes for solvent extraction of Cs.[3,44-58] Work with crown ethers alone have shown problems with stability of the crown ethers. Following initial work by French scientists, Moyer and coworkers have shown that calix(4)arene-bis-(2,3-naptho)-crown-6 in various diluents can selectively extract Cs from acid or alkaline solutions.[56] The diluent differs depending on the pH of the solution. For alkaline solutions, selectivity of Cs over Na exceeds 10,000 compared to 200 for bis-(tert-butylbenzo)-21-crown-7. Selectivity of Cs over K is much lower with a range of 100-900.[56] These selectivities are higher than the selectivities shown by ion exchange materials. The Cs is easily stripped from the solvent by dilute acid. Batch extraction tests with alkaline Hanford waste solution confirmed work with simulants. Only simulants have been tested for acid waste solutions. Testing in centrifugal contactors is underway for simulants of SRS waste. Extensive bench-scale and pilot scale testing will be required for implementation of the technology. The extractant and proprietary diluent modifier are not available on a large scale yet. The process uses very low concentrations in order to minimize overall solvent inventory which minimizes the cost since the extractant is expensive.

III. Tc Separations

A. Past Technetium Separations and Materials

Technetium separations have depended on the pertechnetate ion (TcO_4^-), which is ordinarily the most stable species in aqueous solution. Strong base anion exchange resins such as Dowex^{tm} 1, Purolite^{tm} A520, and others remove TcO_4^- from solution. Other anions such as nitrate, sulfate, and hydroxide compete for the exchange sites. Nitric acid solution >4 M is required to elute TcO_4^- from these resins.

Technetium has been separated by solvent extraction with quaternary amine extractants such as Aliquat^{tm} 336 and others. These extractants are like liquid anion exchange materials with TcO_4^- being extracted by the quaternary ammonium cation function. Technetium is partially extracted in the PUREX process by formation of uranyl pertechnetate.[59] The TRUEX process, which was developed for recovery of transuranium elements from acid waste solutions, also extracts Tc.

B. Recent Developments in Ion Exchange

There have been several recent developments in ion exchange for Tc.[60-63] Schroeder and co-workers have done extensive development with the commercial anion exchange resin Reillex^{tm} HPQ.[60-62] This resin is a strong base resin with a pyridinium functional group rather than an alkyl ammonium group. The pyridinium cation gives the resin greater stability towards oxidation as well as stronger binding of TcO_4^-. Reillex^{tm} HPQ gives high distribution values in batch tests with TcO_4^-. As with other anion exchange resins, nitrate and hydroxide anions compete with TcO_4^- for the exchange sites. An algorithm was developed for estimating the expected distribution between solution and resin for various supernates. The value for the distribution coefficient, K_d, between Reillex^{tm} HPQ and most Hanford waste supernates is in the range of 500-600. The strong bonding makes it difficult to elute the pertechnetate ion from the resin. Even 8 M HNO_3 did not completely remove TcO_4^- from the resin. Rapid and complete elution was demonstrated by reduction of TcO_4^- with Sn(II) in the presence of ethylenediamine. Ethylenediamine complexes the Tc(IV) produced and keeps technetium in solution. Workers at ORNL have developed new anion exchange resins for removal of TcO_4^- from ground water.[63] The resins contain quaternery ammonium functional groups with different alkyl chain lengths attached to the nitrogen. The resins adsorb TcO_4^- so strongly that attempts to elute have been unsuccessful thus far. These resins have not been tested with waste solutions.

During the studies of Reillex resin, Schroeder and co-workers noticed that Hanford tank waste solutions with high organic complexant concentrations showed much lower distribution values than simulants without organics present.[62] Further study has shown that as much as 70 % of the Tc is not present as TcO_4^- in these solutions. They hypothesized that TcO_4^- was being reduced Tc(IV) which was complexed by one of the organic complexants in the solution. Subsequent work by PNNL workers using XAFS showed that the solutions did contain Tc(IV).[64] Studies of other Hanford tank waste solutions show that fresh samples have as much as 15 % of the Tc present as non-pertechnetate species. The identification of the exact compound has not been accomplished due the large number of organic complexants present in the solutions, however, one likely complexant is ethylenediamminetetraacetic acid (EDTA) which has been shown to complex Tc(IV). The Tc can be reoxidized to TcO_4^- if all the organic compounds in solution are oxidized first. Schroeder and co-workers have also shown that silver and persulfate ion can be combined to selectively oxidize Tc without destruction of all the organic compounds in solution.[65] However, complete oxidation requires 0.9 M persulfate ion so that the resulting solution is not compatible with borosilicate glass without removal of the added sulfate.

A different type resin (ABEC-5000tm - Eichrom Industries) was developed, which is easily elutable with water.[66-70] ABEC is an acronym for aqueous biphasic extraction chromatography. Aqueous biphasic extraction involves extraction of metal ions from highly salted solutions with polyethylene glycols (PEG) of varying molecular weight. The low concentration metal ions absorb on the PEG particles in the separate PEG phase. Contacting the PEG phase with water strips the metal ion from the PEG phase. The ABEC resin uses PEG on a macroporous resin support to remove Tc from high salt solutions such as tank waste solutions. Studies with ORNL wastes showed distributions coefficients as high as 927 at equilibrium, which were higher than those for any of the other six resins tested including Reillextm HPQ.[67] Tests with Hanford waste solutions resulted in distribution coefficients that were almost a factor of ten lower than the ORNL results.[64] Irradiation studies show that low molecular weight PEG (<1000) is more stabile than the higher molecular weight materials.

B. Recent Developments in Solvent Extraction

Groups at Argonne National Laboratory (ANL) and ORNL have done extensive studies of Tc solvent extraction with crown ether compounds in hydrocarbon diluents with phase modifiers to increase solubility of the crown ether complexes.[57,71-76] Both groups have found that the crown ether, di-(t-butylcyclohexano)-18-crown-6, works best to extract Sr and Tc. The best diluents appear to be long chain alkyl hydrocarbons with long chain alcohols, cycloketones, and/or tributylphosphate as a modifier to improve solubility of the crown ether and its metal complexes.

The ANL process has been tested at INEEL on simulated acidic wastes.[77] Batch distribution tests allowed design of a process for co-extraction of Sr, Tc and Pb.[77] The solvent, 0.15 M di-(t-butylcyclohexano)-18-crown-6 in 1.5 M TBP/Isopar L, was irradiated to 1000 grays with no measurable change in batch distribution coefficients.[77] Thus the solvent appears to be quite stable to radiation. The ORNL process has been successfully tested in a 12 stage centrifugal contactor with Hanford waste simulant at PNNL.[56] The solvent used in the testing was 0.04 M di-(t-butylcyclohexano)-18-crown-6 in 1.8 M TBP/Isopar L. Both groups are working to combine their Cs solvent extraction processes with their Sr/Tc processes in order to remove all three radionuclides in one process.[56,77] The work is still in progress.

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