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Wastes with the Primary Focus on
Ammonium Molybdophosphate as an
Ion Exchanger: A Literature Review**

C. J. Miller

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Cesium Removal From Liquid Acidic Wastes with the Primary Focus on Ammonium Molybdophosphate as an Ion Exchanger: A Literature Review

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ABSTRACT

Many articles have been written concerning the selective removal of cesium from both acidic and alkaline defense wastes. The majority of the work performed for cesium removal from defense wastes involves alkaline feed solutions. Several different techniques for cesium removal from acidic solutions have been evaluated such as precipitation, solvent extraction, and ion exchange.

The purpose of this paper is to briefly review various techniques for cesium removal from acidic solutions. The main focus of the review will be on ion exchange techniques, particularly those involving ammonium molybdophosphate as the exchanger. The pertinent literature sources are condensed into a single document for quick reference.

The information contained in this document was used as an aid in determining techniques to evaluate cesium removal from the acidic ICPP waste matrices.

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Introduction

The Idaho Chemical Processing Plant (ICPP) reprocessed spent nuclear fuels for uranium recovery until 1992. At this time, the mission of the plant changed to waste management. Radioactive liquid wastes from the uranium recovery process were solidified (at 500°C) in a fluidized bed calciner. The resulting solid is composed of metal oxides, actinides and lanthanides, and fission products.

Liquid waste generated from decontamination and solvent wash activities are stored in tanks for final disposal. This waste is high in sodium content. It was previously blended with raffinates from aluminum and zirconium fuel dissolution and then calcined. Because of the high sodium content, it is not compatible with the calcination process without being blended with aluminum nitrate.

Cesium and strontium are the major heat producers and also the major contributors to the radiation field of the calcine and sodium waste. Both radioactive and non-radioactive cesium are formed in the fission and decay processes and are present in the ICPP calcine and sodium-bearing waste.

There are approximately 600 MCi ^{137}Cs stored in the United States from defense wastes and commercial fuels. This amount is expected to increase to approximately 12,000 MCi (mostly from commercial fuels) [1]. At the Idaho Chemical Processing Plant, there is approximately 3800 m³ of calcined waste stored in stainless steel bins and approximately 1.5 million gallons of

high sodium, acidic liquid waste. This is equal to approximately 0.7 MCi ^{137}Cs and 0.01 MCi ^{134}Cs in the high sodium, acidic liquid waste [2]. The calcined waste contains approximately 8.7 MCi ^{137}Cs and 0.05 MCi ^{134}Cs . Removal of cesium would significantly decrease the radioactivity level of the waste. To decrease the volume of high level waste destined for a repository, removal of radionuclides, including cesium, is required. This paper briefly describes various techniques for removal of cesium from acidic waste solutions. The main focus is on literature describing ammonium molybdophosphate as an ion exchanger. The information contained in this paper aided in the choice to test ammonium molybdophosphate and crystalline silicotitanates for cesium removal from the ICPP wastes.

Removal and Recovery of Cesium from Acidic Solutions

Various cesium removal techniques have been studied and some techniques have been used in large-scale treatment. Some of the procedures that have been evaluated are precipitation, volatilization, solvent extraction, and ion exchange. A brief description of the technologies is given below.

Precipitation Techniques: Precipitation by phosphotungstic acid (PTA) can be performed in acidic (0.5 to 2.0 M HNO_3) media. The phosphotungstic acid concentration does not appear to appreciably influence the reaction efficiency because the phosphotungstic acid is added in excess as a powder. The optimum reaction conditions correspond to 62 mg PTA/mg Cs [3]. The cesium phosphotungstate precipitate is soluble in NaOH solutions, therefore, ion exchange techniques can be used to concentrate and purify the ^{137}Cs from the NaOH solutions [3].

Cesium Volatilization: The volatilization of cesium has been studied as a means of volume reduction by Gay et al. [4]. Less than 10% of the cesium is volatilized at 265°C from Epicor powdered resins and Amberlite bead resins when the resins are loaded with 8920 mg Cs and 8770 mg Cs, respectively.

Volatilization of cesium from Idaho Chemical Processing Plant pilot plant calcines spiked with ^{137}Cs was studied by Brewer and Tranter (1993) [5]. The maximum cesium volatilization achieved was 90 wt% at 900°C for 6 hours. This is well below the amount of cesium removal required to meet Class A requirements.

Cesium volatilization experiments by Del Debbio (1994) [6] show that the volatilization of cesium from pilot plant alumina calcine was 99% while that of pilot plant Fluorinel/Sodium calcine was 99.7%. These values were obtained after heating the calcine at 1000°C for five hours. Cesium removal from pilot plant zirconia calcine was 90% at 1000°C and 99% at 1100°C. The heating time was five hours for this calcine type also. From actual calcine, 96% of the cesium was removed at 1000°C and 99.8% at 1170°C. By increasing the run time from five hours to ten hours, 99% of the cesium can be removed at 1000°C.

Solvent Extraction: Solvent extraction systems have been extensively studied for the removal of cesium from acidic solutions. Heteropolyacids, such as dicarbollide and phosphomolybdic acid, as reagents for the extraction of cesium into nitrobenzene, have been extensively studied by Podesva, Kyrs, and Rais at the Nuclear Research Institute in Czechoslovakia [7,8,9].

Crown ethers have been prepared as ligands for extraction of cesium from an aqueous solution into an organic phase. Crown ethers were first synthesized and investigated by Pedersen [10]. These compounds are unusual in their ability to form complexes with alkali metal salts. The stability depends on the correspondence between the alkali metal ionic diameter and the size of the cavity of the crown [10]. Due to the cavity size-ion matching, cesium is strongly extracted by dicyclohexo-21-crown-7.

Many extraction systems based on crown ethers for the selective removal of cesium from acidic solutions have been studied. Blasius, et al. used adducts of dibenzo-21-crown-7 with NaSbCl_6 in chlorine-containing diluents and nitrobenzene [11]. Kinard and McDowell extracted a cesium salt of di(2-ethylhexyl) phosphoric acid (HEDHP) using dicyclohexano-18-crown-6 and HEDHP in benzene [12]. McDowell, et al. has shown that di-(tert-butylbenzo)-18-crown-6 with didodecyl naphthalenesulfonic acid (HDDNS) in toluene is the most efficient crown ether for the extraction of cesium from nitric acid solutions [13]. Davis, et al. have developed a solvent extraction process for the removal and recovery of ^{137}Cs from strong ($\geq 0.5\text{M}$ HNO_3) acid solutions. Four component organic solutions containing tributylphosphate (TBP), dinonylnaphthalene sulfonic acid (NNS), kerosene, and bis 4,4,5[1-hydroxy-2-ethylhexyl]benzo-18-crown-6 give distribution ratios for cesium $D_{\text{Cs}}=1.6$. However, for zirconium $D_{\text{Zr}}=2.1$ due to the extraction of zirconium by TBP [14].

Ion Exchangers: The major advantage of using ion exchange is good selectivity depending on the resin used. Low equipment maintenance may also be an advantage. Inorganic ion

exchangers such as titanium phosphate, zirconium phosphate, ferrocyanide molybdates, hexacyanoferrate compounds, and ammonium molybdophosphate have been looked at extensively for their application to cesium removal from acidic waste. Polyantimonic acid gives high decontamination factors for both strontium and cesium in acidic media [3]. Problems associated with these exchangers include: (1) the acid salts of tungsten and molybdenum are amorphous (which do not easily go into solution to make final waste forms) and (2) the zirconium and titanium of condensed phosphates easily block up the exchange column if present in the feed in the trivalent state [15]. This creates high pressure drops across the column.

Hexacyanoferrate compounds have been studied extensively as inorganic exchangers for alkali metals in strongly acidic solutions [16,17,18]. These inorganic exchangers have also been studied in highly alkaline waste solutions containing high sodium concentrations [19]. These compounds work as exchangers only on pre-formed precipitates of the complex cyanides. Generally, they are used as precipitating agents. The amount sorbed ranges from 85% for silver hexacyanoferrates to 99.7% for cobalt hexacyanoferrates [17].

Crystalline silicotitanates are a class of inorganic ion exchangers for cesium removal from alkaline or acidic solutions. They are currently synthesized jointly by Sandia National Laboratories and Texas A&M University. They were first prepared and evaluated as catalyst supports in 1991 [20]. Crystalline silicotitanates can separate low parts per million levels of cesium from high sodium alkaline feed solutions. Distribution coefficients of $>10,000$ have been achieved [20]. Crystalline silicotitanates are not currently on an engineered support, therefore,

production scale use is not feasible. Work is currently being performed to 1) scale up the CST production to 1000 kg, and 2) put the CST material on an engineered support.

Smit, et al. revealed the ion exchange properties of AMP for cesium in 1959 [21]. Since that time, the high selectivity of AMP in acidic solutions containing large quantities of electrolytes and the stability of the AMP towards radiation has attracted attention throughout the world. Inert carriers such as silica gel, asbestos, and microporous anion exchangers have been used to improve the column characteristics [22]. In acidic solutions ($\text{pH} < 2$), only those metal ions that form insoluble heteropolyacid salts will exchange significantly with the ammonium ions. These include K, Rb, Cs, Fr, Ag, Hg(I), and Tl(I). Bivalent and trivalent ions adsorb well from solutions of pH 2 to 5 [23]. Studies by Archer and Heslop were done to determine the solubility of AMP in water and acids. AMP dissolves readily in basic solutions. It has a finite solubility in pure water as well as acids [24].

Murthy et al. studied ammonium molybdophosphate in an unspecified acid from 0.2M to 10M. Measurements before and after irradiations of approximately 1MGy showed almost no change in capacity and only slight changes in distribution coefficients [25]. Irradiation of AMP with doses of $5\text{E}+08$ rads has no effect on the mechanical properties of AMP on a silica gel support [26].

Since the ion exchange properties of cesium were revealed in 1959, emphasis has been placed on finding a suitable support. Inorganic supports are preferred over organic supports because 1) they have higher thermal and radiation stability, 2) they often have better chemical stability in

highly acidic solutions, 3) they are more compatible for immobilization in a final waste form (i.e. glass), and 4) they have a slower leach rate in the absence of high salt concentrations and low activity for long term storage.

AMP-asbestos mixtures pack well into columns with no apparent separation or non-uniformity and with favorable flow rates. The advantage of AMP-asbestos columns is that they can "run dry" without danger of air bubbles entering the column bed [27,28]. Asbestos is not a favorable material for production scale columns due to reduced bed capacity per unit volume and compaction of the column beds during operation, giving a variable flow rate [29].

AMP has been incorporated in a silica gel matrix by several different techniques [26, 30, 31, 32]. Silica gel has sufficient chemical, thermal, and radiation stability, has a porous structure allowing relatively fast transport of ions and solutions inside the particles, has suitable mechanical properties, and can be prepared in the form of spherical beads. The sol-gel method allows for exchange of the particles into the silica gel matrix which improves the kinetics because the channels are free. Loss of the active component due to peptization and surface abrasion in column operation should also be reduced [26].

Ammonium molybdophosphate has also been precipitated directly into the Amberlite IRA-900 resinous structure. Columns using this resin have shown favorable flow rates [33,34].

Coarse ammonium heteropolyacid salts have been developed to improve the flow rates and

granulometric size of AMP. This is done by adding ammonium salt solutions to aqueous 12-molybdophosphoric acid. However, it appears that these coarse crystals would not be sufficiently stable when contacted with dilute aqueous solutions [29].

In 1992, Sebesta et al. used modified polyacrylonitrile (PAN) as a binding polymer for ammonium molybdophosphate. The advantages of using PAN are 1) it is easy to modify the physicochemical properties (mechanical strength, porosity, and hydrophilicity), 2) the active component can be embedded in the resin as colloids or very fine particles enhancing the achievable capacity, 3) the final product can be shaped into different desirable forms and, 4) any polymer of acrylonitrile produced industrially can be used, decreasing the cost of the sorbent. The kinetic properties of the ion exchange are not affected by the binding polymer [35, 36].

The capacity for cesium on unsupported ammonium molybdophosphate ranges from 1.6 meq Cs/g AMP [32] to 0.65 meq Cs/g AMP [26]. Faubel and Ali (1986) have found the capacity to be 60g Cs/kg AMP [37]. Most researchers have found the capacity to be 58% to 60% of the maximum or 0.95 meq Cs/g AMP [27,33,38].

Several different ammonium solutions have been tested for cesium elution from AMP.

Ammonium nitrate appears to elute 80% to 95% of the cesium from the AMP using 7.9M and 5M ammonium nitrate, respectively [33, 38]. Ammonium chloride has also been used to elute the cesium from the AMP on silica gel support [26]. Sodium hydroxide solutions have been used to dissolve the ammonium molybdophosphate with the attached cesium. The ammonium

molybdophosphate can then be recrystallized by acidifying the solution [33, 36].

Studies done by Marsh, et al. (1993), showed the selectivity of various elements onto selected absorbers from alkaline and acidic simulated waste solutions. The cesium distribution coefficients for many of these absorbers are listed in Table 1 [39]. Many other commercial resins were tested; however, the distribution coefficients for cesium in both the alkaline and acidic feeds were ≤ 2.0 ml/g. From Table 1, it can be seen that both the Sandia National Laboratory crystalline silicotitanates and AMP-PAN are effective in cesium removal from acidic solutions.

Table 2 is a tabulated comparison of different ion exchange materials. The criterion listed in the table for the various exchangers to be compared against are important to know in ion exchange systems. A brief description of the criterion are given below. The governing factor of an ion-exchange reaction is the electrostatic force of attraction. This is dependent on the relative charge, the radius of the hydrated ion, and the degree of nonbonding interactions [40].

The total capacity of the column is equal to the total number of exchanging groups in the column. The breakthrough capacity is generally reported and is always lower than the total capacity. Breakthrough capacity is dependent upon a number of different variables, such as particle size, filtration rate and solution composition [41].

Selectivity is the ability of the column resin to separate two solutes. It determines the readiness with which two or more substances, which form ions of like charge, can be separated. The

with which two or more substances, which form ions of like charge, can be separated. The

Table 1: Cesium Distribution on Selected Absorbers
Two hour Contact Times

Absorber	Kd_{Cs} (ml/g) Acid feed	Kd_{Cs} (ml/g) Alkaline Feed
SNL/CST 35	1011	277
SNL/CST 111	5021	2708
SNL/CST 69	2279	13
SNL/CST 84	8096	3953
SNL/CST 48	758	2820
SNL/CST 68	2308	Not Tested
Czech AMP-PAN	4072	0.4
Czech M315-PAN	64	177
Czech NiFC-PAN	49	943
Duracil® 230	14	106
Ionsiv® TIE-96 (mod)	9	86
Ionsiv® TIE-96	7.9	84
Duolite® CS-100	1.1	225
SRS resorcinol	4.5	599
Amberlyst®15 Cation	1.3	6.5
Amberlyst®XN-1010	2.2	14
Tannin	1.5	66
Czech Na Y-PAN	1.0	7.8
Titanium Hexacyanoferrate	2.7	80
Cobalt Hexacyanoferrate	5.8	263
Titanium Phosphate	2.4	1.1
Niobium Pentoxide	0.9	5.6
Bone Char	1.0	3.1
TiFC-PSF	2.7	102
CoFC-PSF	5.8	3793

selectivity depends on the nature of the exchanging ions and the nature of the ion exchange resin. The nature of the resin includes the amount of cross-linking, and the nature of the functional groups [42].

The distribution coefficient (K_d) of an ion is a measure of the species partitioning between the aqueous and the solid phases. The ion distribution coefficient represents the affinity for different ions to attach to the resin. The larger the K_d , the more strongly the ion is held [42].

The kinetics of an ion-exchange reaction depend on the following five steps:

- 1) Diffusion of ions through the film adhering to the surface of the resin bead
- 2) Diffusion of ions within the resin particle
- 3) Exchange of counterions at the active site
- 4) Diffusion of the exchange ions back to the surface of the resin bead
- 5) Diffusion of the exchanged ions through the adherent surface film into the bulk of the solution.

In dilute solutions ($<0.001M$) the rate-controlling step is #1. In more concentrated solutions, #1, #2, and #3 are all important in controlling the rate of the reaction [40].

The chemical and physical stability of an ion-exchanger is required for normal functioning of the materials. The material should be chemically inert and not subject to moderate temperature changes. Inorganic exchangers are known to be both radiolytically and hydrolytically more stable than organics. Rapid decomposition of organic resins may occur in the presence of strong oxidizing agents and/or heat.

Table 2: Comparison of Selected Ion Exchange Materials

IX Material	Capacity	Selectivity In Acidic Media	Kd ml/g	pH Range	Temp	Kinetics	Radiation Stability	Chemical Stability	Elution	Safety	Engineer- ed Support	Scale Tested	Reference
SNL/CST 35	ND	High	1011	1-10	23°C	Fast	10 ⁹ rads	stable*	difficult	safe	no	lab	39,44,45
SNL/CST 111	ND	High	5021	1-10	23°C	Fast	10 ⁹ rads	stable*	difficult	safe	no	lab	39,44,45
SNL/CST 69	ND	High	2279	1-10	23°C	Fast	10 ⁹ rads	stable*	difficult	safe	no	lab	39,44,45
SNL/CST 84	ND	High	8096	1-10	23°C	Fast	10 ⁹ rads	stable*	difficult	safe	no	lab	39,44,45
SNL/CST 48	ND	High	758	1-10	23°C	Fast	10 ⁹ rads	stable*	difficult	safe	no	lab	39,44,45
SNL/CST 68	ND	High	2308	1-10	23°C	Fast	10 ⁹ rads	stable*	difficult	safe	no	lab	39,44,45
Czech AMP-PAN ¹	90g/kg	High	4072	0-9	ND	Fast	ND	ND	yes	concern ⁸	yes	lab	39,43
Czech M315- PAN ²	ND	High	64	ND	ND	ND	ND	ND	ND	concern ¹²	yes	lab	39,43
Czech NIFC-PAN ³	0.65 mmole/ ml	High	49	ND	ND	Fast	ND	ND	ND	concern ⁹	yes	Pilot Plant	39,43
Durasil 230 ⁴	ND	Mod	14	ND	ND	ND	ND	ND	ND	safe	yes	lab	39
IONSIV TIE-96 ⁵ zeolite	2meq/g	Mod	7.9	3-12	23°C	Slow	10 ⁹ rads	acid degradates	difficult	safe	yes	lab	39,46
SRS/Resorcinol ⁶	2.85 meq/g	Low	4.5	7-12	35°C	ND	10 ⁶ rads	ND	yes	ND	yes	lab	39,47
Cobalt Hexacyanoferrate	0.35 meq/g	High	5.8	9-12	ND	Fast	ND	ND	no	concern ¹⁰	granular	pilot plant	38,39
CoFC-PSF ⁷	ND	Mod	5.8	ND	ND	Slow	ND	ND	ND	concern ¹¹	yes	lab	39

* stable in bases/not tested for acid stability

ND=not determined or data not available

- 1 composite exchanger-Ammonium molybdophosphate/polyacrylonitrile
- 2 composite exchanger- synthetic mordenite/polyacrylonitrile
- 3 composite exchanger- nickel ferrocyanide/polyacrylonitrile
- 4 Durasil- registered trademark of Duratek Corporation, Columbia, MD
- 5 IONSIV-registered trademark of UOP Molecular Sieves, Moorestown, NJ
- 6 Savannah River Formaldehyde-Resorcinol Resin
- 7 Cobalt Hexacyanoferrate-phenolsulfonic-formaldehyde composite
- 8 ammonium and nitrate are mixed together in process---PAN is organic resin
- 9 hexacyanoferrate is a cyanide based compound---PAN is organic resin
- 10 hexacyanoferrate is a cyanide based compound
- 11 hexacyanoferrate is a cyanide based compound
- 12 PAN is an organic support

Elution is the process of removing absorbed ions [42]. Elution can be done by changing the pH of the eluant, the temperature, the solvent type, or the flow rate.

Conclusions

Ammonium molybdophosphate used as an ion exchanger appears to be an effective technique for removal of cesium from acidic solutions. The advantages of using ammonium molybdophosphate far outweigh the disadvantages. The advantages are:

- rapid rate of sorption equilibrium
- high distribution coefficients in acidic media
- high loading capacity
- high selectivity for cesium in complex matrices
- soluble in alkaline solutions
- elution is possible with ammonium nitrate solutions.

The disadvantages of using ammonium molybdophosphate are:

- it is a microcrystalline structure which is not favorable for column use
- the high loadings of AMP result in high radiation doses and hotspots on the column requiring cooling systems
- heat generation could affect the support (i.e. melt the organic support)

It appears that ammonium molybdophosphate can be added to both organic and inorganic supports. Inorganic supports are preferred because they are more hydrolytically and radiolytically stable. Inorganics are also more desirable for glass/glass-ceramic waste forms.

Ammonium molybdophosphate appears to have more advantages than the other exchangers discussed. The literature cited in this document shows that ammonium molybdophosphate as an ion exchanger is a viable technique for removing cesium from acidic media.

Crystalline silicotitanates are also being examined as viable ion exchangers for cesium removal.

The advantages of using crystalline silicotitanates are:

- rapid rate of sorption equilibrium
- high distribution coefficients in acidic solutions
- high selectivity for cesium in complex matrices
- silicates are desirable in glass waste form

The disadvantages of using crystalline silicotitanates are:

- not soluble in alkaline solutions
- difficult if not impossible to elute
- microcrystalline structure is not favorable for column use
- possible high loadings of CST material will result in high radiation doses and hotspots on the column requiring cooling systems
- heat generation could affect support material (i.e. melt an organic support)

It appears that crystalline silicotitanates can be added to both organic and inorganic supports.

Inorganic supports are preferred because they are more hydrolytically and radiolytically stable.

Inorganics are also more desirable for glass/glass-ceramic waste forms.

Crystalline silicotitanates appear to have more advantages than the other exchangers discussed, except ammonium molybdophosphate. It appears that further experimentation utilizing both

techniques for cesium removal should be pursued. An attempt to overcome the disadvantages of each system should be sought.

The selection of crystalline silicotitanates and ammonium molybdophosphate for further investigation into the removal of cesium from the Idaho Chemical Processing Plant waste solutions was based on much of the literature cited in this document.

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