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REVIEW

A Review of Information on Ferrocyanide Solids for Removal of Cesium from Solutions

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ABSTRACT

Ferrocyanide solids have important applications to the removal of radioactive cesium from nuclear waste solutions. These materials are prepared by mixing soluble ferrocyanides and salts of divalent transition metals or other divalent cations. The simple precipitations most commonly give very fine particles or slimes of variable compositions. Special preparation procedures have been developed to control the compositions or to prepare granular solids suitable for column operation. The removal of cesium from solutions has been measured for many different ferrocyanide solids. Some of these solids show an exchange of K^+, Na^+, or NH_4^+ for cesium, but many show sorptions of cesium without a true ion exchange. The performance for cesium removal is described by measurements of the distribution coefficients for cesium with large excesses of ferrocyanides, the capacity for cesium with excess cesium in solution, and the rates of cesium removal. The chemical and physical stability, the solubility, and the elution or recovery requirements for ferrocyanide solids are important to practical applications. These properties are reviewed along with several of the proposed applications.

1. INTRODUCTION

The selective removal of cesium from solutions by ferrocyanide solids has important applications for many radioactive wastes. The large amounts of wastes now stored in tanks at U.S. Department of Energy facilities require pretreatments as a preparation for final disposal. The most attractive concept is to separate the predominant radionuclides (^{137}Cs, ^{90}Sr, transuranics, and perhaps Tc or Co) into a small, concentrated volume for vitrification and deep geological disposal. A good removal (decontamination) process for these radionuclides would allow a simpler and much cheaper disposal of most of the wastes. Separation of the cesium from the nitrate waste solutions is very important to practical and economical final disposal.

A most promising process for selective removal of cesium from solutions involves reacting the cesium with insoluble metal ferrocyanides. These materials are frequently described as inorganic ion exchangers, but the cesium may be absorbed without a true exchange of cations and a reverse exchange (elutriation) may not be practical. The preparation and use of ferrocyanide solids for removal of cesium from solutions have been studied for about 40 years, but the results are mostly empirical and do not show any simple best procedures or process conditions. The purpose of this review is to collect and present the published information in a form convenient for application to radioactive waste treatments.

Amphlett's (1) book on inorganic ion exchangers briefly mentions the use of ferrocyanides for Cs, Sr, and Eu sorption, but has more information on ammonium molybdophosphate for Cs sorption. A review of synthetic inorganic ion exchangers by Pekarek (2) shows results for many different exchanger compositions and contains 70 references citing work conducted over a 6-year period. Loewenschuss (3) reviewed transition metal ferrocyanides for the decontamination of cesium solutions and cited 62 references for 11 metals. A review of zinc and nickel ferrocyanides by Loos-Neskovic (4) was concerned with their preparation, chemical composition, and structure. Campbell (5) evaluated treatment options for wastes at Oak Ridge National Laboratory (ORNL) without a detailed citation of references.

This current review is organized according to the preparation, properties, characteristics, and procedures important to the practical removal of cesium from waste solutions. When Loewenschuss (3) reviewed this type of information, he presented it in 11 sections according to the metal ferrocyanide compounds and included little information published after 1978.

This review starts with the preparation of ferrocyanide solids by simple precipitations, which commonly give slurries of very fine powders. Because these fine solids can give high decontamination factors for cesium and the amounts of cesium are small, simple batch treatments of wastes and one or a few stages can give useful processes. The advantages of column operation with liquid flow through a fixed bed of granular solids are significant, and preparation of ferrocyanide solids in a granular form has received considerable attention. The performance of both fine and granular solids for removal of cesium from solutions and their other characteristics are discussed. Finally, several different specific applications are reviewed.

2. METHODS OF PREPARATION AND CONTROL OF RESULTS

The insoluble ferrocyanide salts are formed by the reaction of a soluble ferrocyanide (K, Na, or H compounds) with soluble metal salts. Both the chemical composition and the size or characteristics of the solid particle can vary over wide ranges depending on the reaction conditions and procedures. The removal of cesium from solutions by these solids varies with both the chemical composition and the physical properties. Practical application of these solids to removal and concentration of cesium requires suitable chemical and physical stability as well as properties that allow an efficient and very complete separation of solids from the solution. As a result of these requirements, two studies of the same nominal ferrocyanide compound may result in much different conclusions about their suitability for a cesium separation. For many studies, the measurements of chemical compositions and physical properties are not reported, and this severely limits the comparison of results.

Many of the preparations describe simple precipitations and give simple chemical compositions with limited experimental verification. Fewer preparations report measurements of composition, structure, and physical properties. The simple precipitations commonly give fine particles or slimes, and attempts to precipitate or to grow larger ferrocyanide particles by digestion have shown little success. Granular particles suitable for liquid flow through columns have been prepared by either precipitating the solid in the pores of a porous particle or by binding the ferrocyanide into a matrix or composite structure.

2.1. Simple Precipitations

Many of the preparation procedures and results described in the literature assume a simple precipitation reaction:

$$\mathrm{Fe(CN)_6^{4-}} + 2\mathrm{M}^{2+} + x\mathrm{H_2O} \rightarrow \mathrm{M_2Fe(CN)_6}\cdot x\mathrm{H_2O} \qquad (1)$$

A small variation in this simple assumption is to use a $\mathrm{M^{2+}/Fe(CN)_6^{4-}}$ ratio of <2 mol/mol and then assume enough Na, K, or H in the product to give an ionic balance. All the precipitation products can be represented by an average composition or a general formula:

$$\mathrm{A}_{2n}\mathrm{M}_{2-n}\mathrm{Fe(CN)_6}\cdot x\mathrm{H_2O} \qquad (2)$$

where A = Na^+, K^+, other alkaline metals, H^+, or perhaps NH_4^+
M = divalent transition metal or divalent cations like UO_2^{2+}, TiO^{2+}, etc.
n = 0, 1, or 2 for simple compositions of definite formulas

Many of the precipitation products show average compositions that do not agree with the integral values of n. There are many indications of products with the composition $A_2M_3[Fe(CN)_6]_2 \cdot H_2O$. Many of the other average compositions appear to be mixtures of hydrates of $A_2MFe(CN)_6$ and $M_2Fe(CN)_6$.

The general formula for the average composition of ferrocyanide solids allows a considerable number of product compositions. Four different cations for A and over a dozen for M give more than 50 combinations. Values of n commonly vary from 0 to 1 and less commonly are from 1 to 2. The physical properties, such as particle size and surface area, also affect the performance for the removal of cesium from solutions. The results for precipitation of ferrocyanide solids and for tests of cesium sorption are too complex for any simple description and explanation. Instead, specific examples of the more carefully done studies will be reviewed as examples.

Three different procedures have been commonly used to supply insoluble ferrocyanide solids for removal of cesium from waste solutions. For a given nominal composition of precipitate, the three procedures can give much different compositions and physical properties. One procedure is to mix the ferrocyanide solution into the waste solution for an "in-situ" preparation of the solids. The Co, Ni, Zn, or other transition metal components may be components of the waste or may be added as salt solutions. This procedure is not very suitable for caustic wastes because most transition metals are not soluble at high pHs and would also precipitate as hydroxides. A second procedure is to premix the ferrocyanide and metal salt solutions to precipitate a slurry and then add the slurry to the waste solution. The third procedure is to precipitate the slurry and then separate, wash, dry, size classify, or otherwise pretreat the solids before adding them to the waste. This last procedure can be used to modify and improve the physical properties of the solids, but the treated solids often show reduced decontamination factors (DFs) or capacities as compared to the freshly prepared slurries.

Loos-Neskovic (4) reviewed the preparation methods, compositions, and structures for zinc and nickel only as the M cations. That review shows 53 references and over 90 tabulated results for ferrocyanides containing zinc or nickel. The reviewed resulted in only a few generalizations, including distinct differences between those for zinc ferrocyanides as compared to those for nickel ferrocyanides. The quantitative results are few, and contradictory results are common.

The precipitation results for zinc ferrocyanides show products with definite formulas. Most commonly reported are $Zn_2Fe(CN)_6 \cdot xH_2O$ and $A_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$. Kawamura (6) used varying ratios of sodium ferrocyanide and zinc nitrate to prepare either of the pure compounds or mixtures. The compounds for $n = 1$ are reported for K and Cs [$K_2ZnFe(CN)_6 \cdot xH_2O$ and $Cs_2ZnFe(CN)_6 \cdot xH_2O$] but not for other A cations. Vlasselaer (7) used potassium ferrocyanide and an excess of zinc sulfate to prepare $K_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$. An excess of zinc salt and sodium or lithium ferrocyanide resulted in formation of $Zn_2Fe(CN)_6 \cdot xH_2O$ only (8, 9). A Zn/Fe ratio of 1.5 is favorable to a high yield of $A_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$. A near stoichiometric yield is possible when A is sodium, but other cations for A give mixtures.

While the copper ferrocyanides do not show the definite compositions found for the zinc ferrocyanides, the $Cu_2Fe(CN)_6 \cdot xH_2O$ composition can be prepared using an excess of copper salt and $Na_4Fe(CN)_4$ (10). Using potassium ferricyanide and an excess of copper salt gave the corresponding ferricyanide, $Cu_3[Fe(CN)_6]_2$.

The precipitation of cobalt ferrocyanides can give many different average compositions which are commonly described as being mixtures. Prout used an excess of cobalt salt and controlled precipitation conditions in order to prepare granular ferrocyanide solids (11). His results indicated that the nominal $K_2CoFe(CN)_6$ was a mixture of $Co_2Fe(CN)_6$ and some $K_4Fe(CN)_6$. Lehto (12) prepared a $K_2CoFe(CN)_6$ composition by adding the cobalt nitrate solution slowly to a $K_4Fe(CN)_6$ solution. The reverse order of mixing gave compositions of n from 0.29 to 0.98 for the potassium cobalt ferrocyanide solids.

Most other precipitated ferrocyanide solids show compositions with nonintegral values of n and limited indication of definite formulas. Krtil (13) used an excess of uranyl nitrate, and the precipitate showed U:Fe to be 1.6:1.

2.2. Composition, Structure, and Analytical Measurements

Measurements of the properties of ferrocyanide solids are reviewed here with two exceptions: the performance of the ferrocyanides for removal of cesium in solution is in Section 3, and the review of simple precipitations (Section 2.1) included many results on compositions. All compositions can be represented by the average compositions or formulas shown by Eq. (2). There may be definite compounds corresponding to $n = 0.5$ with the formula $AM_3[Fe(CN)_6]_2 \cdot xH_2O$.

Barton (14) recognized that zinc gave definite compounds, $Cs_2ZnFe(CN)_6$ and $K_2ZnFe(CN)_6$, with sharp x-ray diffraction patterns, while the solids with nickel or copper in place of zinc did not. Valentini (9), by chemical and thermogravimetric analyses, showed a formula of $Zn_2Fe(CN)_6 \cdot 2\frac{1}{2}H_2O$. Prout (11) used an excess of $Co(NO_3)_2$ solution and carefully controlled conditions to prepare a granular solid, but the product appeared to be a mixture of compounds with atom ratios of K:Co:Fe of 1.6:1.4:1.0. Lee (15) reports chemical analyses in agreement with a formula $K_2Cu_3[Fe(CN)_6]_2 \cdot 4H_2O$ but concluded that this might be a mixture of $K_2CuFe(CN)_6$ and $Cu_2Fe(CN)_6$ compounds. Lee (16) analyzed six ferrocyanide solids and decided that five were heterogeneous and one might be a definite $Cu_2Fe(CN)_6 \cdot 2\frac{1}{2}H_2O$ compound. Valentini (10) used excesses of $CuSO_4$ solution to prepare dried precipitates that analyzed $Cu_2Fe(CN)_6 \cdot H_2O$ and $Cu_3[Fe(CN)_6]_2 \cdot 14H_2O$. Heterogeneous mixtures of compounds were reported for cobalt ferrocyanides (17) and nickel and zinc ferrocyanides (18). Lehto (12) slowly added $Co(NO_3)_2$ solutions to $K_4Fe(CN)_6$ solution to prepare pure $K_2CoFe(CN)_6$. The reverse order of mixing gave heterogeneous mixtures.

The composition results indicate that the zinc ferrocyanides are usually definite compounds. Controlled precipitations with excesses of the critical solution can give $Cu_2Fe(CN)_6$ or $K_2CoFe(CN)_6$ compositions. All other ferrocyanide precipitates are probably heterogeneous mixtures.

The early information on the structures of the ferrocyanide compounds is reviewed by Sharpe (19). Most compounds of formula $A_2MFe(CN)_6$ have face-centered cubic unit cells with a primary cell parameter (a) of ~10.1 Å. Loos-Neskovic (8) reports cubic, rhombohedral, trigonal, and mixtures of crystal structures for different compositions of zinc and magnesium ferrocyanides. The crystal structures for some compositions are listed in Table 1.

Additional analytical and physical measurements are reported for only a small fraction of the many ferrocyanides tested for sorption of cesium. Many of the earliest studies were empirical tests of cesium sorption vs preparation procedures with poor or no measurements of composition and properties. A review by Pekarek (2) of ferrocyanides as ion exchangers lists 91 references and a small amount of information describing composition and structure as the only properties to correlate with the ion-exchange characteristics. Some analytical and physical measurements are listed in Table 2.

The ferricyanide compounds with $[Fe(CN)_6]^{3-}$ in place of $[Fe(CN)_6]^{4-}$ for ferrocyanides may also be used to remove cesium from solutions. The

TABLE 1
Ferrocyanide Crystal Structures vs Compositions

Compound reported	Crystal structure: Type[a]	Crystal structure: Cell parameter (Å)	Ref.
$Cs_2ZnFe(CN)_6$	F.c. cubic	10.2	14
$Zn_2Fe(CN)_6 \cdot 2\frac{1}{2}H_2O$	Rhombic		9
$Ni_2Fe(CN)_6 \cdot xH_2O$	Cubic	10.1	8
$Cs_{1.65}Zn_{1.14}Fe(CN)_6 \cdot xH_2O$	Cubic	10.36	8
$A_{2n}Ni_{2-n}Fe(CN)_6 \cdot xH_2O$	F.c. cubic	10.2	18
$K_2CoFe(CN)_6 \cdot xH_2O$	F.c. cubic		11
$K_{2n}Co_{2-n}Fe(CN)_6 \cdot xH_2O$	F.c. cubic		11
$Na_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$	Rhombohedric		20
$Zn_2Fe(CN)_6 \cdot 2H_2O$	Trigonal		20

[a] F.c. = face-centered.

ferrocyanide compounds are easily oxidized to ferricyanides by nitric acid of ≥1 M concentrations. Mehra (22) prepared and measured properties of ferricyanide solids. The ferricyanides have no particular advantages, but they are usually more soluble, which is a disadvantage. They also tend to have lower capacities since there is only one easily exchangeable cation instead of the two that occur in ferrocyanides.

2.3. Precipitation on Porous Supports

The most common objective for this procedure is to substitute the physical properties of the support particle (size, shape, physical stability) for

TABLE 2
Analytical and Physical Measurements for Ferrocyanide Solids

Report composition	Density (g/cm^3)	Surface area (m^2/g)	Other measurements	Ref.
$Zn_2Fe(CN)_6 \cdot 2\frac{1}{2}H_2O$	1.78			9
$K_2Cu[Fe(CN)_6] \cdot xH_2O$	2.27	18.4	Pore volume = 8.8%	15
$K_{2n}Co_{2-n}Fe(CN)_6 \cdot H_2O$	2.12, 2.20			21
$K_{1.70}Co_{1.12}Fe(CN)_6 \cdot H_2O$		62	Crystallite diameter, 30 to 50 nm	17
$Na_{2x}Ni_{2-x}Fe(CN)_6$		45 to 75	Particles of 0.06 μm	8
$Zn_2Fe(CN)_6 \cdot 2H_2O$		28 to 39	Particles of 0.2 μm	8
$Na_2Zn_3[Fe(CN)_6]_2$		30		8
$K_{2n}Co_{2-n}Fe(CN)_6$		60 to 200	Crystallites of 10 to 40 nm	12

the undesirable physical properties of the pure ferrocyanide solids. The support particle can be selected to have good size and shape properties for operation of ion-exchange columns. The disadvantages of the porous support particle include:

1. The capacity is reduced by the mass or volume occupied by the support material.
2. The kinetics of the ion exchange may be slower and controlled by the mass transfer within the particle.
3. The ferrocyanide solids occupy pore volume and can result in a final particle of low porosity and poor ion-exchange rates.
4. The support material may be a significant added cost for the initial supply or for the final disposal.

Several chemically unreactive solids have been used as supports for ferrocyanide precipitates. After reviewing these results, Konecny (23) chose silica gel supports for additional studies. The porous silica gel particles were first loaded with $K_4Fe(CN)_6$ by a series of contact with solutions and with drying between contacts. The particles were then reacted with $ZnSO_4$ or other metal salt solutions and dried at room temperature. Chemical analyses indicated the same precipitate compositions as reported in the previous section for simple precipitations. The metal ferrocyanide loadings were 0.10 to 0.31 g/g of silica gel for single precipitations and 0.28 to 0.45 g/g silica gel for repeated precipitations. The result of tests using these materials for removal of cesium from solutions are included in Sections 3 and 4. Valentini (24) added 40-mesh silica gel to $CuSO_4$ solution and then added $Na_4Fe(CN)_6$ solution with stirring. The dried gel contained $Cu_2Fe(CN)_6 \cdot H_2O$; some samples were oxidized to copper ferricyanide by 1 M HNO_3 before use.

Macroreticular ion-exchange resins are porous particles with good properties for operation of exchange columns. An anion resin can be converted to the ferrocyanide form by reaction with $K_4Fe(CN)_6$ solution. This ferrocyanide resin can be reacted with metal salt solutions to precipitate the metal ferrocyanides in the resin pores. Up to 10 repetitions of this procedure were used to prepare products that were 64 wt% nickel ferrocyanide (25). A combination of this precipitation and a similar precipitation of calcium phosphate can give a product that will remove both cesium and strontium.

Using a porous support that reacts to form the ferrocyanide solids offers the possibility of minimizing the amount of inert porous support materials. Hydrous titanium oxide gel spheres were reacted with ferrocyanide solutions to form titanium ferrocyanides (26). The gel sphere shape and particle size were retained throughout the reactions with ferrocyanide and cesium solutions. The product $Fe(CN)_6^{4-}$/Ti ratios were 0.7 mol/mol using $K_4Fe(CN)_6$ + HCl solution and 0.82 mol/mol using $H_4Fe(CN)_6$ solution. One overnight treatment with solutions of $K_4Fe(CN)_6$ + HCl gave an unexplained high value of 2.82 mol/mol and a correspondingly high capacity for cesium.

Other nonreactive supports such as fiberglass, paper pulp, carbon, and clay generally did not give good packed beds for column operation. Fine solids either plugged the bed pores or were lost to the effluent solution.

2.4. Formation of Controlled Sizes of Larger Particles

Larger particles of ferrocyanide solids would be desirable for operation of ion-exchange columns and might also show better chemical or physical stability in some solutions. Several special procedures were tested for preparation of large ferrocyanide granules or spheres. The kinetics of the ion exchange will depend on the mass transfer within the particle and is slower as the particle size increases. There is also a tendency for preferential reaction of the surface, and the average capacity may decrease as the specific surface area decreases.

A precipitation procedure was developed to give a granular $K_2CoFe(CN)_6$ after drying to 115°C that could be crushed and sized for use in columns (11, 27). The same procedure did not give suitable granular products for any other sodium or potassium ferro- or ferricyanide salts of Zn, Mg, Cd, U, Fe, Ni, Cu, or Cr. These other precipitates were colloidal fines and/or dried to fine powders. The precipitation and drying conditions were important to the preparation of a granular solid instead of a powder. The recommended conditions were a slow addition of $K_4Fe(CN)_6$ solution to a cobalt salt solution at 15°C with an excess of the cobalt salt. The precipitate was centrifuged, washed with water, and dried at about 120°C. The chemical analyses indicated a mixture of $Co[CoFe(CN)_6]$ and $K_2[CoFe(CN)_6]$. Campbell (28) prepared granular solids by this procedure and demonstrated a much improved chemical stability as compared to powder for pHs of 11 to 13.

One special preparation procedure to give larger particles is slow growth of the insoluble ferrocyanide on the surface of potassium or sodium ferrocyanide crystals (20). The crystals are mixed with concentrated solutions of nickel or zinc nitrate or other metallic salts. The insoluble zinc or other metal ferrocyanides grow on the surface by diffusion of ions. The solution concentrations and other conditions must be carefully controlled to maintain a flux of both reactants to form the insoluble ferrocyanide on the surfaces of the particles. Nonoptimum conditions gave weak beads which are fragile and break into fragments. Optimum conditions gave hollow spheres that were stable (no change in pressure drop) for 20,000 column volumes of liquid flow through a column.

The fine ferrocyanide powders from a simple precipitation might be formed into larger particles by use of an organic binder or cement. One procedure tested was to make a paste of zinc ferrocyanide powder using an organic solvent and organic binder, dry at 80°C, crush, and size (29). Granules prepared with polystyrene in chloroform to give 20 wt% binder after drying showed constant flows of 0.5 M NH_4NO_3 solution (no degradation) for 240 hours in a column.

Some results are reported for mixing of ferrocyanide powders into a liquid organic and formation of macroporous ion-exchange resin beads. Narbutt (30) implanted a titanium ferrocyanide with good chemical properties for sorption of Cs into a formaldehyde–phenol cation-exchange resin.

Collins (31) incorporated either ferrocyanide solids or soluble ferrocyanides into the feed fluids for a gel sphere preparation of hydrous titania gels. The particle size and shape can be controlled to be optimum for liquid flow through columns. The capacity for cesium and the rates of reaction are both reduced as compared to those of fine ferrocyanide powders.

One procedure also reviewed in Section 2.3 is to react a porous solid to form a ferrocyanide compound. Partial reaction leaves a porous support for the ferrocyanide solids, while a complete conversion would give a porous ferrocyanide particle. Caletka (26) reacted hydrous titanium oxide particles with ferrocyanide solutions. The original gel sphere shape and particle size were retained throughout the conversion to titanium ferrocyanide and the adsorption of Cs. One product showed a high conversion to ferrocyanide and a high capacity of 2.6 meq Cs/g. Caletka (32) describes the preparation of titanium and five other hydrous oxide gel spheres and their reaction with $H_4Fe(CN)_6$ and other acids.

3. REMOVAL OF CESIUM FROM SOLUTIONS

After a ferrocyanide solid of controlled and known composition and structure has been prepared, its performance for removal of cesium from solutions must then be determined experimentally. The mechanism of cesium removal can vary from a true, relatively fast ion exchange to a much slower change in chemical structure. Intermediate rates and mixed mechanisms are often observed. The performance of a solid for cesium removal is commonly described by three measurements: 1) distribution coefficient, K, to measure the equilibrium cesium concentrations with an excess of solids, 2) capacity measurement of how much cesium will be removed by a unit amount of solids with an excess of cesium in the solution, and 3) rate measurement of how rapidly the cesium reacts with the solid. All of these depend on other variables such as the concentration of cesium in solution, the concentration of other cations, the pH, and the temperature.

3.1. Mechanism of Cesium Adsorption

The mechanism by which the ferrocyanide solids remove cesium from solution are complex and dependent on both the composition and the physical properties of the solids. The results may indicate different mechanisms for the same metal ferrocyanide prepared by different procedures.

An ion exchange of Cs for K or Na is usually shown by the appearance of stoichiometric amounts of K or Na in solution and rapid reaction to equilibrium. Lee (15) studied the mechanism for granular solids of average composition $K_2Cu_3[Fe(CN)_6]_2 \cdot 4H_2O$. His results show K releases to solution that are a little larger than the Cs sorbed and very small releases of Cu to solution. Lee (21) looked at other compositions and found that two potassium cobalt ferrocyanides sorbed Cs by ion exchange with K, while $Cu_2Fe(CN)_6 \cdot 2\frac{1}{2}H_2O$ sorbed Cs without releasing Cu to the solution. Lehto (17) found an ion exchange of Cs for K using $K_2[CoFe(CN)_6]$, and a small release of Co corresponding to the amount of $Co[CoFe(CN)_6]$ in the solids. Vlasselaer (7) and Loos-Neskovic (18) found a 1-to-1 Cs/K exchange for $K_2Zn_3[Fe(CN)_6]_2$ without any release of Zn. For $Zn_2Fe(CN)_6$, the Zn released was much smaller than the Cs sorbed and the crystal lattice changed from a trigonal structure to a cubic structure. Equilibrium was approached in several hours, while the K/Cs ion exchange approached equilibrium in 10 minutes.

In general, the K^+ and Na^+ in ferrocyanide solids show a true ion-exchange behavior with Cs^+. The simple ferrocyanides like $Cu_2Fe(CN)_6$, $Zn_2Fe(CN)_6$, and $Co_2Fe(CN)_6$ show complex mechanisms with releases of Cu^{2+}, Zn^{2+}, or Co^{2+} that are either small or much less than the amount of Cs^+ sorbed.

3.2. Distribution Coefficient

The distribution coefficient (K) is an equilibrium ratio of concentrations. Neglecting any losses (to container walls, etc.), a material balance gives K for a batch equilibrium as

$$K = \frac{(C_0 - C)V}{mC} \tag{3}$$

where C = equilibrium concentration in solution
C_0 = initial concentration in solution
V = amount of solution
m = amount of solids

A decontamination factor, *DF*, is

$$DF = \frac{C_0}{C} = 1 + \frac{mK}{V} \tag{4}$$

Results are often reported as percent removals, which are related to *K* or *DF* as follows:

$$\%\ \text{removed} = \frac{100(C_0 - C)}{C_0} = 100\left(\frac{DF - 1}{DF}\right) = \frac{100}{\frac{V}{mK} + 1} \tag{5}$$

Most ferrocyanide solids give high distribution coefficients for Cs. The determination of these distribution coefficients by measuring a small residual solution concentration contains troublesome sources of error. The cesium concentrations are usually determined from the radioactivity of a cesium tracer. This measurement may be high (and thus give low values of *K*) as a result of:

1. Cesium remaining as unremoved colloidal ferrocyanide solids instead of soluble cesium
2. Cesium remaining in a nonreactive form, such as a complex or colloidal polymer
3. A small amount of radiation from an impurity that is significant after most of the cesium is removed and that is measured as cesium by the procedures used
4. An incomplete equilibrium. Liquid/solid ratios of 10^3 to 10^4 are unfavorable for easy equilibration

The cesium distribution coefficients are dependent on so many variables, including the composition of the solution; the composition of the solids; and the amount of cesium, temperature, etc., that exact comparisons are difficult. Some common sources of error (discussed above) give low values of *K*, and many of the measurements are low approximations of the true distribution coefficients. Examples of some reported values are in Table 3.

Campbell (28) measured distribution coefficients at concentrations that simulate those for a proposed application. Distribution coefficients were measured for several nickel and cobalt ferrocyanides using simulated waste tank supernate concentrations and *m*/*V* ratios in Eq. (1) of 10 to 100 ppm. Most values of *K* were 0.5×10^6 to 4×10^6. Low values of 10 ppm for *m*/*V* and pHs above 11 gave lower values for *K*, probably as a result of the decomposition or solubility of the ferrocyanide solids for these conditions. The ferrocyanides were stable and remained effective

TABLE 3
Some Experimental Measurements of Cesium Distribution Coefficient

Ferrocyanide solid	Solution	pH	K (mL/g)	Ref.
$K_{2n}Co_{2-n}Fe(CN)_6$, n = 0.77 to 0.85	Water	6	5×10^4	17
$K_{1.70}Co_{1.12}Fe(CN)_6$	0.04 M Na	1 to 8	2×10^5	33
$K_{2n}Co_{n-2}Fe(CN)_6$	2 to 4 M Na, 0.25 M K	9.5	$(0.9 \text{ to } 3) \times 10^6$	28
	2 to 4 M Na, 1.0 M K	9.5	2×10^5	
$Na_{2n}Ni_{2-n}Fe(CN)_6$	2 to 4 M Na, 0.25 M K	9.5	$(2 \text{ to } 3) \times 10^6$	28
	2 to 4 M Na, 1.0 M K	9.5	$(7 \text{ to } 10) \times 10^5$	
$Na_{0.47}Cu_{1.67}Fe(CN)_6$	5 M Na		$>10^5$	34
$K_{2n}Co_{2-n}Fe(CN)_6$	5 M Na		$>10^5$	
$K_{1.49}Cu_{0.25}Co_{0.96}Fe(CN)_6$	0.04 M Na	1 to 8	3×10^4	33
	2.7 M Na	1 to 12	$\sim 2 \times 10^4$	
$K_2Zn_3[Fe(CN)_6]_2$	<0.001 M K	3	10^3	7
$Zn_2Fe(CN)_6$	0.05 M HNO_3		3×10^3	7
Titanium ferrocyanide	0 to 0.1 M HCl	1 to 3	$(1 \text{ to } 3) \times 10^5$	35
Titanium ferrocyanide	Water	7	5×10^4	36
	1 M HNO_3		10^4	
	1 M $NaNO_3$		5×10^3	
Uranium ferrocyanide	0.1 to 1 M HNO_3		$(1 \text{ to } 10) \times 10^4$	13

for low pHs down to 1 M acid. The distribution coefficients decreased with an increase in potassium concentrations from 0.25 to 1 M, but 2 to 8 M sodium concentrations had little effect.

Lehto (33) also measured the cesium distribution coefficients for two ferrocyanide compositions and ranges of pH, potassium concentrations, and sodium concentrations. His results covered a wider range of variables (Figs. 1 to 3) and agreed with those of Campbell (28). The cesium distribution coefficients decreased with increasing potassium concentrations, but showed little dependence on sodium concentrations. pHs of 2 to 9 had little effect, but higher pHs decreased the distribution coefficient.

3.3. Capacity

The capacity of the solids for cesium is the amount of cesium retained after complete reaction or saturation. For slow flow through a long ion-exchange column, the capacity is indicated by the breakthrough point. It can also be determined by a long-time equilibration of a small amount of solids with an excess of Cs in the solution.

The simple theoretical cesium capacity of a ferrocyanide solid is 2 mol/mol ferrocyanide. This capacity assumes that one of the M cations is fixed in the structure and the remaining cations are exchangeable.

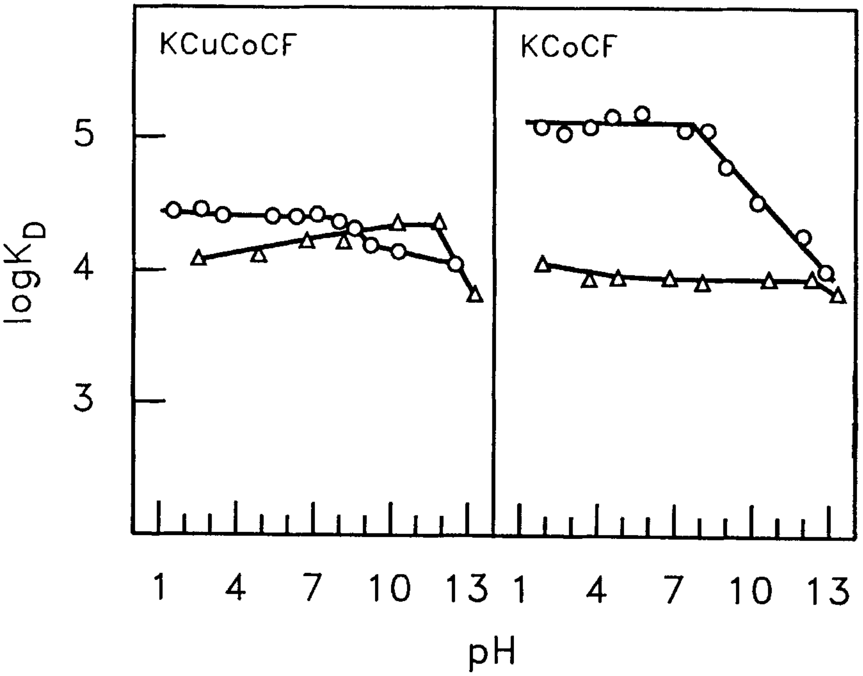

FIG. 1 Distribution coefficient (K_D) of ^{137}Cs on KCoCF or KCuCoCF from nuclear waste solutions as a function of pH. (○) = waste solution I ([Na^+] = 4.35 mmol/L, [K^+] = 1.2 mmol/L). (△) = waste solution II ([Na^+] = 2700 mmol/L, [K^+] = 240 mmol/L). Batch factor, 100 mL/g. Grain size of hexacyanoferrates, 0.07–0.140 mm. [From Lehto (33), CF indicates ferrocyanide.]

Another capacity estimate is $2n$ mol/mol ferrocyanide for $n \leq 1$ in $A_{2n}\ M_{2-n}Fe(CN)_6$. This capacity assumes that the alkaline metals, H^+ or NH_4^+, are exchangeable and the divalent cations are not. These two capacities are upper limits for ion exchange and are rarely realized in practice. For $n = 0$ or all divalent cations, the sorption of cesium is usually by a sorption instead of an ion-exchange mechanism and the capacities are unpredictable.

The capacity results reported in reviews illustrate the wide variability with composition and preparation conditions. Pekarek (2) lists capacities of 0.4 to 2.1 mol Cs/mol ferrocyanide for 13 compositions. Loos-Neskovic (18) found reports of 0.91 to 2.1 mol Cs/mol Fe for zinc ferrocyanides, 0.35 to 1.9 mol Cs/mol Fe for nickel ferrocyanides, and 0.3 to 2.1 mol Cs/mol Fe for other ferrocyanide solids. Kourim (37) claimed near theoretical

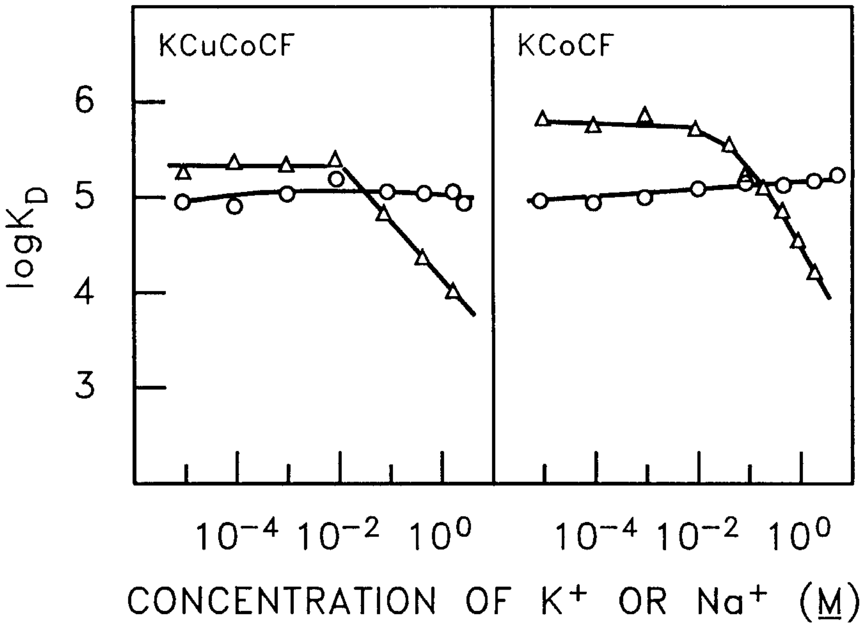

FIG. 2 Distribution coefficient (K_D) of ^{137}Cs on KCoCF or KCuCoCF as a function of Na^+ (O) and K^+ (Δ) concentrations. Batch factor, 100 mL/g. Grain size of hexacyanoferrates, 0.07–0.14 mm. [From Lehto (33), CF indicates ferrocyanide.]

capacities for cesium on Zn, Cu, Ni, Co, and Fe(III) ferrocyanides, but lower values are more commonly reported.

The preparation procedures selected to control the physical properties of the solids often reduce the capacities for cesium. Prout (11) prepared granular potassium cobalt ferrocyanide and reported capacities of about 0.2 mol Cs/mol ferrocyanide. Loos-Neskovic (38) prepared particles larger than 100 μm by a slow growth procedure. The maximum cesium capacities were 0.9 to 1.0 mol Cs/mol Fe for zinc ferrocyanides and 0.4 to 1.0 mol Cs/mol Fe for nickel ferrocyanides. Konecny (23) precipitated ferrocyanides in silica gel and found capacities of 0.25 to 1.3 mol Cs/mol ferrocyanide. Both the highest and lowest values were for zinc ferrocyanides. All these special preparations give lower ranges of capacities than for fine powders of the same compositions. Stejskal (29) used an organic binder for ferrocyanide powders with little or no effect on the capacities for cesium.

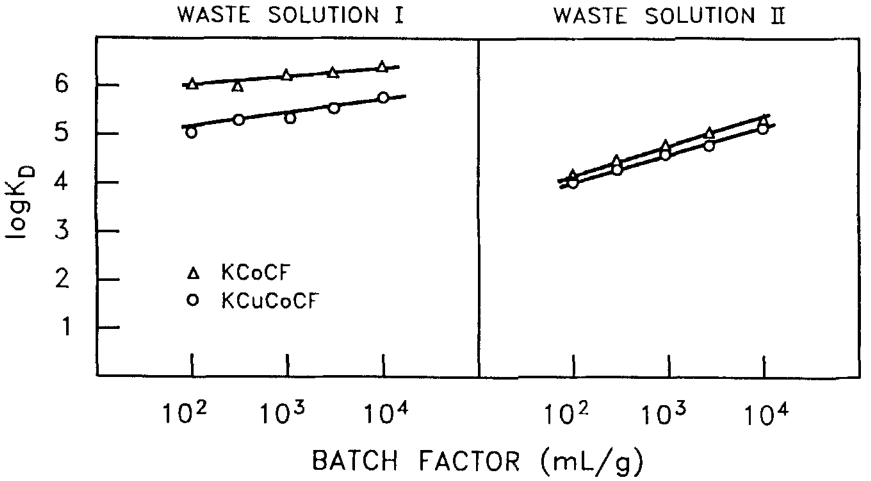

FIG. 3 Distribution coefficient (K_D) of ^{137}Cs on KCoCF or KCuCoCF as a function of batch factor from waste solution I ($[Na^+]$ = 17 mmol/L, $[K^+]$ = 2.2 mmol/L, pH 9.0) and waste solution II ($[Na^+]$ = 2700 mmol/L, $[K^+]$, 240 mL/L, pH = 13.0). Grain sizes of hexacyanoferrates, 0.07–0.14 mm. [From Lehto (33), CF indicates ferrocyanide.]

Lehto (12) correlated the capacities of potassium cobalt ferrocyanides with the surface area of the solids. He assumed an exchange for the surface layer only and 0.25 nm^2 for each cesium atom. Both capacity and surface area correlated with n for a series of compositions of $K_{2n}Co_{2-n}Fe(CN)_6$. The minimum in capacity and surface area was for $n \approx 0.8$, and this composition showed the maximum in crystallinity by x-ray diffraction. Lehto showed agreement with the compositions and capacities reported by four other authors for potassium cobalt ferrocyanides. All these capacities are from 0.15 to 0.8 mol Cs/mol ferrocyanide.

With only a few exceptions, the high capacities for cesium were for the zinc and copper ferrocyanides. For the production of ^{137}Cs gamma sources (14), a high capacity to give a high specific activity was the most important requirement. Zinc ferrocyanide approached the theoretical capacity of 2 mol Cs/mol ferrocyanide [$Cs_2ZnFe(CN)_6$], while Ni, Cu, and Fe all had capacities of ~1 mol Cs/mol ferrocyanide. Vlasselaer (7) found that $K_2Zn_3[Fe(CN)_6]_2$ showed a complete exchange for potassium and no exchange of zinc, or a capacity of 1 mol Cs/mol ferrocyanide. Lee (15) found a capacity of 0.86 mol/mol ferrocyanide for a solid of average composition $K_2Cu_3[Fe(CN)_6]_2 \cdot 4H_2O$. This is equivalent to a nearly complete exchange of potassium, but no copper. Caletka (26) reacted hydrous titanium oxide spheres with ferrocyanide solutions. Most of the products showed only partial conversions to titania ferrocyanides and capacities of 0.2 to 0.5 mol Cs/mol ferrocyanide. One product from reaction with $K_4Fe(CN)_6$ + HCl solution showed a much higher conversion and a capacity of 2.6 mol Cs/mol ferrocyanide.

3.4. Rates of Reaction

Several different rates may be important or controlling for the sorption of cesium from solutions. The cesium in the bulk solution must be transferred to the solid surface, and this transfer is commonly controlled by diffusion through a liquid film on the solid surface. Transfer within the solid is important after the surface layer is reacted. True ion-exchange reactions are commonly fast, but other chemical reactions may be much slower.

A careful study of the kinetics of cesium sorption on a $K_2Cu_3[Fe(CN)_6]_2 \cdot 4H_2O$ solid was reported by Lee (21). For a low cesium concentration of 2.8×10^{-6} M, liquid film diffusion was controlling with a diffusion coefficient of 1.465×10^{-9} m^2/s at 20°C. The dependence of the diffusion coefficient on temperature indicates an activation energy of 15.14 kJ/mol. The results for much higher cesium concentrations of 3.8×10^{-3} M do not appear to agree with diffusion in the solid as a controlling mechanism. A model based on chemical reaction as the controlling rate and a progressive shell mechanism gives a much better fit of the experimental data. The temperature dependence indicates an activation energy of 74.85 kJ/mol, which is within the typical range for chemical reactions. The experimental results show a brief, high initial rate of cesium sorption which does not fit this progressive shell chemical reaction model. This high initial rate may result from the porosity and high surface area of the ferrocyanide solids.

The rates of reaction for cesium sorption can vary greatly with the composition of the ferrocyanide solids. These differences result from differences in the removal mechanisms (Section 3.1). Loos-Neskovic (18) measured and discussed these differences for nickel and zinc ferrocyanides. The $Zn_2Fe(CN)_6$ solids required several hours to approach equilibrium as compared to <10 minutes for $Na_2ZnFe(CN)_6$ or $K_2ZnFe(CN)_6$. Similar rate results for these two compounds were also reported by Kawamura (6). The solution concentrations showed a simple ion exchange with removal of cesium from solution and replacement by the same molal amounts of Na or K. The $Zn_2Fe(CN)_6$ did not show a replacement of zinc by cesium, and x-ray diffraction showed a change in structure during sorption of cesium. In general, the sorption of cesium was rapid by an ion-exchange mechanism when the ferrocyanides contained K^+, Na^+, H^+, or NH_4^+, but was much slower for $M_2Fe(CN)_6$ compositions. Loos-Neskovic (38) later reported results for additional ferrocyanide compositions and for sorption of Cs, Ag, and Pd. All sorptions showed high rates for trace amounts, but the rates for larger amounts varied with both the ferrocyanide compositions and the cation sorbed.

Some discussions of rates of reaction are not easily compared because of additional variables. Prout (11) used conditions to form a granular potassium cobalt ferrocyanide. His times of 1 hour to approach equilibrium are probably controlled by the diffusion in the large granules. Faubel (39) found very high rates for an ammonium cobalt ferrocyanide and a much slower rate for a potassium nickel ferrocyanide, but the preparation procedures are not comparable. Lehto (33) reported fast rates for two ferrocyanides, but the rates were much slower for concentrated (high alkali metal) solutions than for dilute solutions.

4. OTHER CHARACTERISTICS IMPORTANT TO PRACTICAL OPERATION

In addition to the preparation of a good particle that reacts well with cesium, some other characteristics of the ferrocyanide solids are also important to practical operation. The solid must not degrade excessively at the process conditions used. Chemical decomposition or physical degradation separately or together must not be excessive. Any solids entrained with the treated solution will limit the *DF*s for cesium. If all of the cesium is removed from solution, but 0.01% of the solids are entrained, the apparent *DF* could not exceed 10^4. Concentrated loadings of ^{137}Cs can result in high radiation exposures. Low solubilities of ferrocyanide solids are necessary because solution/solid volume ratios of 10^3 or 10^4 are commonly used. Some applications, such as recycle of pressurized-water reactor (PWR) coolant water, require very low limits on the concentrations of $Fe(CN)_6^{4+}$ or iron.

4.1. Chemical Stability

The efficient removal of cesium from solutions requires that there be little chemical decomposition of the ferrocyanide solids during contact with the solution and the separation of solids. The waste solutions from fuel reprocessing and those from dissolution of waste tank sludges will have low pHs (high acid concentrations). Many waste tanks contain neutralized and concentrated wastes; the supernate above the settled solids have high salt concentrations and high pHs. Some processes to separate strontium require high pHs, and it would be convenient to make the cesium separation at the same pH.

Most applications of the ferrocyanide solids are to treat dilute solutions of cesium using large solution/solid volume ratios. It would be convenient and more practical to treat the solutions with a minimum amount of dilution or concentration adjustment. For this reason, the chemical stability of ferrocyanide solids has been studied at many different solution concentrations. The results are difficult to evaluate in quantitative terms. Results are most commonly expressed as the concentration that first results in significantly less effective removal of cesium from solutions. These concentration limits may also be given in terms of the useful or allowable concentration ranges. For example, Loos-Neskovic (20) described the chemical stability of zinc and nickel ferrocyanides. Zinc ferrocyanides can be used from pH 1 to 10; nickel ferrocyanides from pH 0 to 12. Organic solvents, such as acetone, can be used. The products were tested between 20 and 60°C.

The ferrocyanide solids are chemically decomposed at either high caustic or high acid concentrations and are oxidized to the ferricyanides by nitric or other oxidizing agents. Some example reactions are:

$$Cs_2CoFe(CN)_6 + 3H_2SO_4 \rightarrow Cs_2SO_4 + CoSO_4 + FeSO_4 + 6HCN \qquad (6)$$

$$Cs_2CoFe(CN)_6 + 6NaOH \rightarrow 2CsOH + Co(OH)_2 + Fe(OH)_2 + 6NaCN \qquad (7)$$

$$3Fe(CN)_6^{4-} + 4H^+ + NO_3^- \rightarrow 3Fe(CN)_6^{3-} + NO + 2H_2O \qquad (8)$$

All of the ferrocyanide solids were chemically stable over a pH range from about 11 maximum to moderately acid solutions. The caustic decomposition reaction (Eq. 7) takes place above pH 11, but the rate is dependent on the solid preparation procedure. Fine powders lose effectiveness very rapidly, but granular potassium cobalt ferrocyanide prepared according to the procedure of Prout (11, 27) is stable for periods of hours to several days up to pH 13. Campbell (28) found that low ferrocyanide concentrations at pH 10 give a maximum in cesium *DF* at 1 day; this result shows significant decomposition at pH 10. This maximum in cesium *DF* is not detectable at higher concentrations of the ferrocyanides. Campbell also found that potassium copper ferrocyanide lost effectiveness more rapidly than potassium cobalt ferrocyanide as the pH increased. Campbell found effective removal of cesium down to pH 2, even for high salt concentrations, but a nickel compound was better than the cobalt compound, and the Cs *DF*s decreased as the pH decreased. Faubel (39) found good retention of Cs by Co or Ni ferricyanides at pHs above 7.5, but the retentions were very poor in 1 M or concentrated HNO_3. Valentini (9) observed much different adsorption behavior for cesium on $Zn_2Fe(CN)_6$ from NH_4NO_3 solutions as compared to HNO_3 solutions. The behavior in NH_4NO_3 can be explained by ion-exchange mechanisms. The behavior in HNO_3 solution is affected by oxidation to ferricyanide to release zinc and by decomposition of the ferro- or ferricyanide compounds.

4.2. Physical Stability

The good physical properties that are present in freshly prepared ferrocyanide may be lost during use. Such losses that are caused by the chemical environment are reviewed in the previous section. Losses by simple dissolution are determined by the solubility (see Section 4.3). Some other important causes of lack of physical stability are radiation damage, high temperatures, and mechanical erosion from flow or mixing effects.

A principal advantage of inorganic ion exchangers is that they can usually tolerate much higher radiation exposures than can organic exchangers. Nuclear fuels are usually allowed to decay before reprocessing, and the wastes have commonly decayed for long periods before treatment to remove cesium. As a result, the radiation damage to ferrocyanide solids by ^{137}Cs is small for normal processing times. The radiation damage by other radioisotopes is generally insignificant. Phillips (40) reported that copper ferrocyanide shows no effects from radiation exposures up to 10^7 MGy. Watari (41) reported no change in cesium removal capability after a 10^7-R (from ^{60}Co) dose to iron ferrocyanide precipitated in an anion-exchange resin. Barton (14) reported that cesium zinc ferrocyanide slurries of high cesium content did not show radiation decompositions for a week (17 Ci/g of ^{137}Cs).

The metal ferrocyanides show weight losses during heating, which are waters of hydration followed by losses of CN or oxidation, depending on the atmosphere. Valentini (10) showed that $Cu_2Fe(CN)_6 \cdot 12H_2O$ in nitrogen lost $11H_2O$ by 145°C and decomposed to ferrous and copper cyanides at 425°C. In air at 185°C, oxidation gave copper oxide, $(CN)_2$, and ferriferrocyanide.

For many of the initial preparations of ferrocyanide solids, the formation of slimes or very fine particles was a major problem. If these initial fines were eliminated by changes in the preparation procedures or by sizing treatments, then the remaining particles could usually be used without further release of fines. Some attempts to use ferrocyanides deposited on other solids, such as carbon or asbestos, were exceptions and showed continuing releases of fine particles.

4.3. Solubility

Most separations of cesium are for solutions containing low concentrations of cesium; the solution/solid ratios are commonly 10^3 to 10^4 L/kg, and the solubility of the ferrocyanide solids must be very low to limit losses. For some applications with use of the decontaminated solutions (for example, recycle to reactor cooling systems), very low solubilities are necessary to meet the low concentration limits necessary. The ferrocyanide solids can also decompose chemically, and the chemical decomposition losses and solubility effects may be difficult to identify separately. In addition to the more complete chemical decomposition, ferrocyanides can be oxidized by nitric acid (see Section 4.1 on chemical stability) or other oxidizing agents to ferricyanides. Valentini (9) reported a low solubility for zinc ferrocyanide and higher solubilities for the cobalt and nickel compounds without giving values. Narbutt (42) studied the removal of cesium for recycle of PWR coolant. Titanium ferrocyanides gave the lowest solubilities, and this compound, formed in ion-exchanging resins or in titania gel particles, showed solubilities $<3 \times 10^{-6}$ mol $Fe(CN)_6^{4-}$/L.

4.4. Elution or Recovery

A basic concept of ion-exchange separations is that the ion exchange is reversible to allow collection of a product in solution and reuse of the ion-exchange material. This type of elution or recovery of the ferrocyanide solids used to collect cesium has not been practical. All of the chemical treatments that give good removal of cesium from the solids also give a chemical attack on or degradation of the ferrocyanide.

For typical uses of ferrocyanides to produce ^{137}Cs for gamma sources (14) or for analytical measurements (43), the conditions used to recover the cesium as solutions also decompose the ferrocyanides. Konecny (23) used several different ferrocyanides, precipitated on several silica gels, and only eluted 47 to 72% of the cesium with the exception of 90% for one sample of copper ferrocyanide. Lee (15) reported that desorption of cesium by nitric acid was 80% as a maximum and was a destructive process with both disintegration to give fines and oxidation to ferricyanide. Prout (11) was unable to find a satisfactory elution procedure. The most effective eluant solutions were mercury or thallium nitrate, but both partially decomposed the ferrocyanide solids. Stejskal (29) tested zinc ferrocyanide and found deterioration of the mechanical properties and losses of 50 to 70% of the original cesium capacity after 2 to 6 cycles.

An incomplete stripping of an ion-exchange material and any decomposition or disintegration are highly likely to result in unsatisfactory operation for the next loading cycle. Any ion-exchange fines that leave with the solution will tend to give increased losses or lower *DF*s for the ion to be removed. Fines will foul the flow passages between the bed particles in a packed bed and give excessive pressure drops. Based on the presently available information, all uses of ferrocyanide solids to remove cesium from solution must be based on one cycle with complete replacement of the cesium-loaded solids.

5. APPLICATIONS

Most of the experimental studies of ferrocyanide solids for reaction with cesium have been prompted by specific applications. The different types of applications have different requirements that result in large differences in the recommended compositions, procedures, and results. Even when the applications have many similarities, the small differences result in different conclusions. For some applications, the products are the solids containing cesium. For others, the important product is a well-decontaminated solution, and the cesium-loaded solids are a waste requiring disposal. Information concerning specific applications of the ferrocyanide solids is reviewed here.

5.1. Collection of Cesium for Analytical Measurements

A large fraction of the early studies of ferrocyanide solids to separate cesium from solutions were concerned with analytical determinations of cesium or ^{137}Cs in natural waters. Many different ferrocyanide solids were easily prepared and showed the high *DF*s and the required selectivity for cesium. The differences in results were mainly empirical demonstrations of physical properties and procedures that were convenient for large volumes of freshwater or seawater. The reviews by Pekarek (2) and Loewenschuss (3) include many references to these studies. Many of the results are cited in Sections 2, 3, and 4 of this review. While simple batch mixing using fine solids gave useful results, the advantage of flow through columns containing granular solids was commonly recognized. Watari (43) demonstrated efficient column operation by precipitating copper ferrocyanide in a macroreticular anion-exchange resin. Valentini (24) demonstrated efficient column operation by precipitating the copper ferrocyanide in the pores of 40-mesh silica gel. Either flow-through columns with 10^3 to 10^4 bed volumes or good separation after batch mixing with similar ratios of solids to water is required. Collection efficiencies for cesium were determined using spiked samples of known concentrations. Efficiency values of 95 to 98% were used as correction factors and were acceptable considering the overall accuracy needed. The references for analytical applications are useful to confirm the preparation and *DF* for different compositions but usually provide little information on capacity or on the other characteristics important to applications for nuclear waste solutions.

5.2. Production of ^{137}Cs Gamma Sources

The separation of cesium from acidic PUREX wastes was a production application of ferrocyanide solids (14). This application differs from waste treatment processes in that the product is the concentrated cesium instead of the decontaminated solutions. A high specific activity (concentration of cesium) in the solids is important, but a high *DF* for the solution is not. Based on experience and preliminary experiments, the first separations tested were with nickel ferrocyanide and 2.5 M HNO_3 in the feed waste. The purity of the separated cesium was limited by interference by iron, uranium, and some fission products. Neutralization with NaOH or ammonia can precipitate the iron, and this iron precipitate scavenges many of the fission products. When nine ferrocyanides and ferricyanides were tested at these higher pHs, zinc ferrocyanide gave the highest cesium content. The results indicate a definite $Cs_2ZnFe(CN)_6$ compound with a low solubility and a sharp x-ray diffraction pattern. The nickel and other ferrocyanide solids gave lower cesium contents with compositions corresponding to $Cs_2Ni_3[Fe(CN)_6]_2$ or $CsNiFe(CN)_6$. The nickel ferrocyanide removed cesium over a much wider pH range than the zinc ferrocyanide, but was less effective than zinc ferrocyanide at its optimum pH. The overall result illustrates the importance of optimizing all the process conditions together. The small-scale chemical flow-sheet studies for recovery of cesium were reported by Moore (44) and Van Tuyl (45). The ferrocyanide-type processes were later replaced by other inorganic ion-exchange processes using zeolites that allowed column operation with easy elutriation and many cycles of use (46).

A similar production of cesium gamma radiation sources was reported by Filippov (47). The preferred adsorbent was potassium copper ferrocyanide on silica with an average composition of $KCu_{1.5}Fe(CN)_6 \cdot nSiO_2 \cdot mH_2O$, with n equal to 3 to 6 and m equal to 4 to 8. The cesium was elutriated with nitric acid and the adsorbent reconditioned for reuse by treatment with sodium sulfite–potassium chloride solutions. Similar potassium-zinc and potassium-nickel ferrocyanides on silica gel were much less satisfactory for desorption and reuse.

5.3. Decontamination of Dilute Solutions

For decontamination of dilute solutions (e.g., PWR coolants), a well-decontaminated solution is the desired product and the ferrocyanide solids loaded with cesium are a waste for disposal. High *DF*s may be needed, and high capacities are desirable to minimize the waste volumes of solid waste. The requirements for selectivity and chemical stability may be much less severe than for decontamination of waste tank supernates.

Narbutt (42) identified the solubility of the ferrocyanide compound as a critical requirement. Titanium ferrocyanides with high Ti/Fe ratios (apparently largely hydrous titania) demonstrated very low solubilities and also were granular particles with good mechanical properties for use in packed columns. The best results were for a titanium ferrocyanide formed in a cation-exchange resin. This material demonstrated very low solubilities, good *DF*s for up to 10^4 bed volumes, and good resistance to radiation damage. A titania sol–gel particle gave good preliminary results.

Lehto (33) also studied ferrocyanides for two PWR wastes (dilute solutions and an alkaline evaporator concentrate). The decontaminated solutions were wastes for disposal, and the solubility of the ferrocyanides was not highly important. Lehto demonstrated good column operation for 12,800 bed volumes using a solid of composition $K_{1.49}Cu_{0.25}Co_{0.96}Fe(CN)_6$.

Gutman (48) used preformed copper ferrocyanides in combination with membrane filtration to decontaminate pond wastewater. The concentrated slurry was settled and centrifuged to give an overall volume reduction of 15,000 (volume ratio of wastewater:concentrated slurry).

5.4. Decontamination of Waste Tank Supernates

The removal of ^{137}Cs from waste tank supernates at U.S. DOE production plants has very severe requirements. The cesium radioactivity is the predominant gamma radioactivity, and good decontamination factors (commonly about 10^4) are needed. Capacity and rates of reaction are important because large volumes must be treated with large volume reductions. High caustic or acid concentrations in these wastes result in chemical decomposition of ferrocyanides.

There are no full-scale or pilot-plant demonstrations of ferrocyanide solids for the decontamination of waste tank supernates. The production of ^{137}Cs (Section 5.2) did not require high recoveries or *DF*s and had other special requirements. Development studies by Campbell (28) and Faubel (39) used small amounts of simulated waste solutions or a few milliliters of real waste supernates. These results are included in Sections 3 and 4 but do not provide engineering information. Burns (49) described the in-situ formation of nickel and other ferrocyanides with settling in the waste tank to allow discharge of millions of gallons of wastes to the ground (cribs). After many years, the chemical reactivity of these ferrocyanide slurries was recognized to be a hazard and has been studied experimentally (50). The removal of ^{137}Cs was very good, but the accumulated ferrocyanide solids in the waste storage tank now produce large periodic discharges of H_2 and nitrogen oxide gases (51). These discharges are now a severe hazard and problem, and the ground discharge of the decontaminated solutions is also no longer acceptable.

In summary, the chemical performance and other characteristics of ferrocyanide solids appear to be excellent for removal of cesium from waste supernates, and these results have been confirmed with small-scale tests with a few milliliters of real waste solutions. But the problem of final disposal has not been adequately solved, and practical flow sheets remain undemonstrated for both pilot-plant and plant-scale operation.

5.5. Final Disposal Options

The usual procedure for ion-exchange materials is to elutriate or regenerate, and thus reuse, the material for many cycles. The regeneration results for the cesium-loaded ferrocyanides all show chemical attack or physical degradation that is too severe to allow repeated cycles. Granular particles prepared by precipitation on a porous support or as ferrocyanide solids in a matrix do not degrade as severely physically but show large losses of capacity.

Another disposal option is long-term storage of cesium-loaded ferrocyanide solids. Since storage times are much longer than normal process times, the radiation damage from ^{137}Cs will be 10^3 to 10^4 greater and is a significant problem. Beaven (52) reported results for disposal of copper ferrocyanides as 33.3 wt% loadings in cement. The samples containing ferrocyanides give homogeneous waste forms with adequate strengths and low cesium leach rates.

The most promising disposal options involve the chemical decomposition of the cesium ferrocyanides to give more stable solids compatible with conventional HLW disposal procedures. Campbell (5) suggested a caustic digestion to leave metal hydroxides. Schulz (53) patented a fusion with carbonates and oxides to incorporate the metals into a leach-resistant glass.

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