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Studies on Sorption of Radiocesium on Copper-Hexacyanoferrate-Loaded Resins

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Studies on Sorption of Radiocesium on Copper-Hexacyanoferrate-Loaded Resins

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ABSTRACT

Copper hexacyanoferrate(II) was incorporated in the matrix of the strongly basic anion-exchange resin Indion-810 for the sorption of radiocesium from aqueous solutions. Its efficiency for the removal of cesium was tested under both static and dynamic conditions. The resin was found to be highly selective for radiocesium from a variety of salt and acid solutions. With the help of x-ray diffraction patterns, infrared spectrometry, thermal gravimetry, and differential thermal analysis, the interaction of copper hexacyanoferrate(II) with the quaternary amine of Indion-810 resin was investigated. Pilot-scale studies using this resin indicated that radiocesium can be effectively removed from thousands of bed volumes of spent fuel storage bay water.

INTRODUCTION

Among various inorganic ion-exchange materials exhibiting selective sorption properties for radiocesium, the hexacyanoferrates of transition elements have been studied (1–7) extensively due to the stabilizing effect of the large cesium ion on the crystal structure of the sorbent. Copper hexacyanoferrate(II) is reported to be more suitable, especially for routine applications, because of high cesium recovery and good mechanical stability (8). All the products prepared so far by precipitation methods have a large proportion of very small particles and offer too low a permeability to be of any use for column work. The development of the metal cyanoferrate for use on an industrial scale depends on a low cost of the product with large stable particles. This led many investigators to use several types of supports such as bentonite (9) and silica gel (10, 11). Because the results were often not reproducible and differed from author to author, these attempts have had limited success.

In order to overcome the above difficulties, attempts were made to load anion-exchange resins with metal salts of interest. Kazakov (12) and Karpova (13) loaded copper hexacyanoferrate on AV-17 and AN-9 type anion exchangers whereas Watari (14) used Amberlite-904 for this purpose. Our earlier investigations (15) with two macroreticular strong base anion-exchange resins indicated the suitability of Indion-810 for loading metal salts of interest. This paper describes the preparation, characterization, and ion-exchange properties of copper hexacyanoferrate(II) loaded on Indion-810. The interaction of organic matrices with loaded salts has also been investigated. Their applications in the treatment of large volumes of low level radioactive waste solutions, which have received little attention so far, were also looked into.

EXPERIMENTAL

Indion-810 resin (50 g) in chloride form was converted to the hexacyanoferrate(II) form by repeated treatment with a 250-mL solution of 0.5 M potassium hexacyanoferrate(II). This was thoroughly washed with distilled water and treated with a 500-mL solution containing 1 M $Cu(NO_3)_2$ and 0.5 M KNO_3 for 3 hours. The resin was finally washed with distilled water to make it free from dissolved salts, air dried, and stored. For multiple salt loadings, the once-loaded resin was retreated with two 250-mL portions of 0.5 M potassium hexacyanoferrate(II) solution, and copper hexacyanoferrate(II) was loaded again by the same procedure described above. The treatment was repeated, and the multiple-loaded copper hexacyanoferrate(II)s are designated as RCuCF-I, RCuCF-II, and RCuCF-III.

The copper hexacyanoferrate(II) contents of the resins were determined by decomposing the resins by heating with concentrated sulfuric acid and hydrogen peroxide. Fe(III) and Cu(II) were determined by inductively coupled plasma (ICP) emission spectroscopy. Potassium was measured by flame photometry. The densities of the resins in different forms were measured by a standard method (16). The batch capacities of the resins were determined by contacting 0.5 g of each resin with two portions of 20 mL of 0.01 N $CsNO_3$ containing cesium-134 as a tracer for 6 hours. The aqueous phases were counted for their gamma activities.

The batchwise distribution measurements were performed by shaking 0.1 g of the exchanger with 10 mL of the appropriate solution containing cesium-134 or any other suitable radioisotope as tracer by a mechanical shaker for 6 hours, which was found to be sufficient for attaining equilibrium. The aqueous phase was separated by centrifugation and counted for gamma activity. Gamma activity measurements were carried out in a well-type NaI(Tl) detector connected to a single channel analyzer whereas beta activity was measured by using a G.M. counter. The results are expressed in terms of the distribution coefficient (K_d), which is defined as

$$K_d = (1 - p)V/pm$$

where p is the fraction of the residual radioisotope in the aqueous phase, V is the volume of the solution in milliliters, and m is the sorbent weight in grams.

A weighed amount (1.5 g) of the resin was packed in a glass column of 0.5 cm diameter. Solutions containing 50 ppm of cesium traced with cesium-134 were passed through the column at different flow rates using a peristaltic pump. The results are expressed in terms of % breakthrough:

$$\% \text{ Breakthrough} = (C_i/C_0) \times 100$$

where C_i is the activity in the ith effluent and C_0 is the activity in the feed.

The x-ray diffraction patterns of the powdered resin samples and pure copper hexacyanoferrate(II) were obtained with CuKα radiation. The infrared spectroscopy measurements were made with a Perkin-Elmer 1618 spectrometer for which a few milligrams of the sample was powdered, mixed with KBr, pressed, and then spectra recorded. The DTA and TGA of the various samples were recorded at a constant heating rate of 5°C/min in the presence of air.

RESULTS AND DISCUSSION

Some physicochemical properties of these loaded resins are summarized in Table 1. These results show that the maximum amount of copper hexacyanoferrate(II) which can be loaded on Indion-810 is 0.387 mg/g of the resin, which is achieved in the third loading only. Density measurements showed that the resins became heavier after loading, and these values can be used for characterizing the loading of metal salt. The maximum capacity measured for cesium was 0.36 meq/g of resin, which is rather low as compared to the theoretical values.

TABLE 1
Physicochemical Characteristics of Loaded Resins

Sorbent	Density (g/cm^3)	CUCF loading % (w/w)	Batch capacity Cs (meq/g)
RCF	1.10	—	—
RCuCF-I	1.21	17.2	0.12
RCuCF-II	1.29	38.4	0.35
RCuCF-III	1.29	38.7	0.36

The distribution coefficients of cesium ion and some other multivalent ions were measured and are presented in Table 2. The results indicate that the single-loaded sample (RCuCF-I) is highly specific for cesium ions, but affinity for multivalent ions in general is low. The double-loaded sample (RCuCF-II) recorded higher distribution coefficient values for all ions and particularly for Co(II) and Ce(III), which may be due to the presence of some residual unreacted cyanoferrate(II) ions in the resin matrix leading to ion pair formation with these ions. These results show that RCuCF-I is suitable for separation of cesium ions from solutions in the presence of multivalent ions whereas RCuCF-II exchanger is more useful when the exchanger is required to remove multivalent ions along with cesium ions.

The time for attaining equilibrium with distilled water traced with radiocesium by RCuCF-I and RCuCF-II was studied, and the results are presented in Fig. 1. They show that the rates of reaction for cesium sorption can vary greatly with the composition of the cyanoferrate solids. Sorption is fairly rapid in the initial stages, probably due to surface ex-

TABLE 2
Distribution Coefficient (K_d) of Different Metal Ions with RCuCF-I and RCuCF-II

	Distribution coefficient (K_d)	
Metal ion	RCuCF-I	RCuCF-II
Cs(I)	1.27×10^5	1.89×10^5
Sr(II)	33.49	54.97
Co(II)	150.62	9.56×10^4
Ce(III)	95.29	2853.01
$Ru(NO)^{2+}$	35.90	9.07

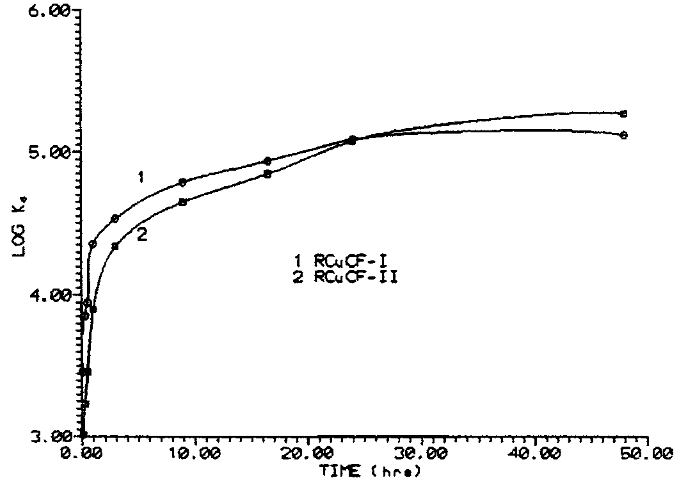

FIG. 1 Time dependence of sorption of cesium on (1) RCuCF-I and (2) RCuCF-II.

change, followed by a slow step controlled by mass transfer within the particle (17). It was seen that although RCuCF-II recorded higher distribution coefficient values for cesium, the time required to reach equilibrium is also higher.

The effect of competing ions such as Na$^+$ K$^+$, NH$_4^+$, and H$^+$ on the sorption of radiocesium on RCuCF-I was studied, and the results are presented in Fig. 2. They indicate that Na$^+$ and K$^+$ ions up to 1 M concentration have a marginal effect on cesium uptake whereas the effect of NH$_4^+$ ion is more pronounced. The tolerance of this resin to large chemical loads points toward its utility in the treatment of waste streams loaded with salts, such as process and regenerant wastewaters. This resin may also be profitably used in the treatment of salted reprocessing waste after adjusting the pH of the waste to 8–10. However, nitric acid in concentrations >0.1 M had a more drastic effect on the distribution coefficients of cesium, and there seemed to be a slight oxidation of the metal salt to hexacyanoferrate(III) as indicated by the change of color to yellow.

The results of the column experiments with RCuCF-I are presented in the form of breakthrough curves in Fig. 3. Due to the very high distribution coefficient (K_d) value recorded by this resin with cesium ions, the curves are very steep and sharp. There is little loss in the breakthrough capacity as the flow rates increase from 10 to 40 bed volumes per hour.

Kazakov and Karpova (18), while investigating the interaction of amine groups with copper hexacyanoferrate(II) in soluble amines in organic

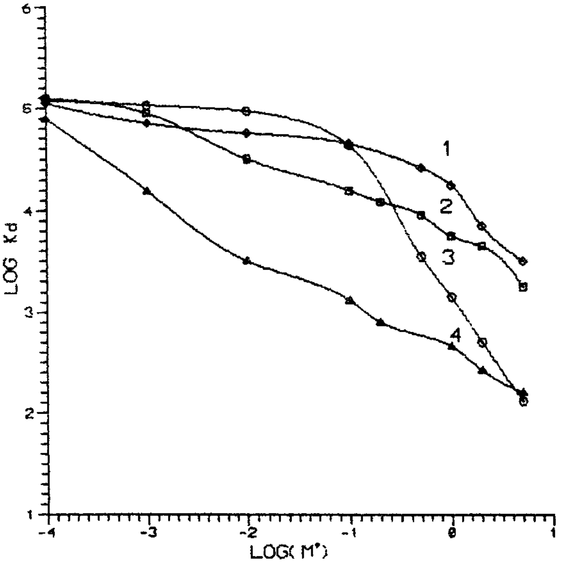

FIG. 2 Distribution coefficient (K_d) of cesium as a function of acid/salt concentration. Curve 1, Na^+; Curve 2, K^+; Curve 3, H^+; and Curve 4, NH_4^+.

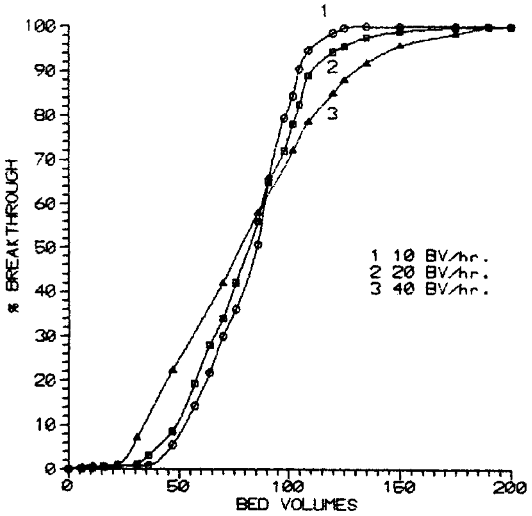

FIG. 3 Breakthrough curves for cesium uptake on RCuCF-I.

phases, indicated the formation of cyanoferrate-organic ionites. We carried out a series of measurements to investigate whether there is any interaction between the quaternary amine part of the Indion-810 resin with copper hexacyanoferrate(II) loaded on it resulting in a chelate-type intermolecular compound or if the inorganic ion exchanger is just physically occluded in the resin matrix in the void spaces provided by the macroreticular resin.

In order to determine the nature of the ionogenic complex of resin-copper hexacyanoferrate(II), x-ray powder diffraction patterns of the single-loaded resin (RCuCF-I) were recorded along with pure copper hexacyanoferrate(II). In Fig. 4, Curves 1, 2, and 3 are the XRD patterns of pure copper hexacyanoferrate(II), RCuCF-I, and RCF, respectively. Comparison of the patterns reveals that there is almost complete loss of the crystal-

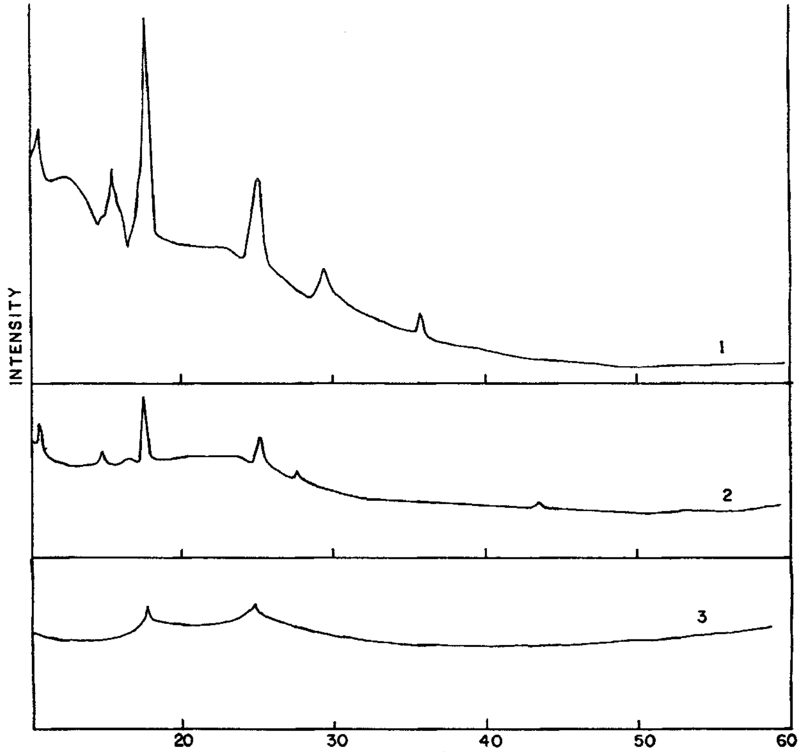

FIG. 4 X-ray diffraction pattrens of (1) copper hexacyanoferrate(II), (2) RCuCF-I, and (3) RCF.

line phase of copper hexacyanoferrate(II) when it is loaded on the resin, indicating that the loaded copper hexacyanoferrate(II) is now part of the polymer matrix due to its linkage to the amine part of the exchanger.

Figure 5 compares the IR spectra of pure copper hexacyanoferrate(II) with the single-metal-salt-loaded resin RCuCF-I. Special attention was paid to the two absorption bands in the 400–600 cm^{-1} range which correspond to the Fe—C stretching and Fe—C≡N bending modes around 580 and 414 cm^{-1}, respectively. It was noticed that in single-metal-salt-loaded resin RCuCF-I there is a shift and breakup of the band at 580 cm^{-1} into two bands which can be attributed to the decreased symmetry of the $Fe(CN)_6^{4-}$ ion due to the interaction of the R_4N^+ resin group with copper hexacyanoferrate(II) in the matrix.

The thermograms in Fig. 6, Curves 1, 2, and 3 show the weight losses between ambient to 500°C of pure copper hexacyanoferrate(II) powder (CuCF), Indion-810 in the cyanoferrate(II) form (RCF), and copper hexacyanoferrate(II) loaded on the resin (RCuCF-I), respectively. Figure 6 indicate that the first weight loss occurring between ambient and 180°C is due to the loss of two water molecules of $K_2CuFe(CN)_6 \cdot 2H_2O$. At about 220°C the decomposition of anhydrous $K_2CuFe(CN)_6$ starts; it is completed by 260°C as indicated by an exothermic peak in the DTA (Fig. 6, Curve 1). As postulated by Lehto (19), the decomposition can be

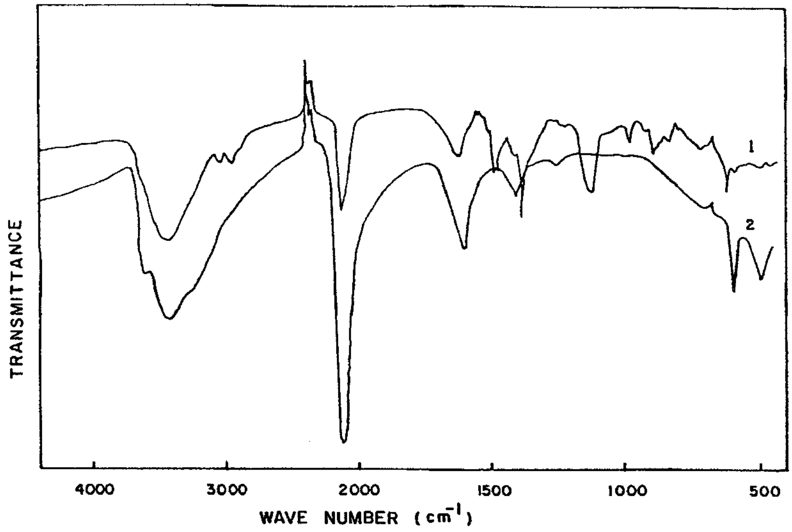

FIG. 5 IR spectra of (1) RCuCF-I and (2) copper hexacyanoferrate(II).

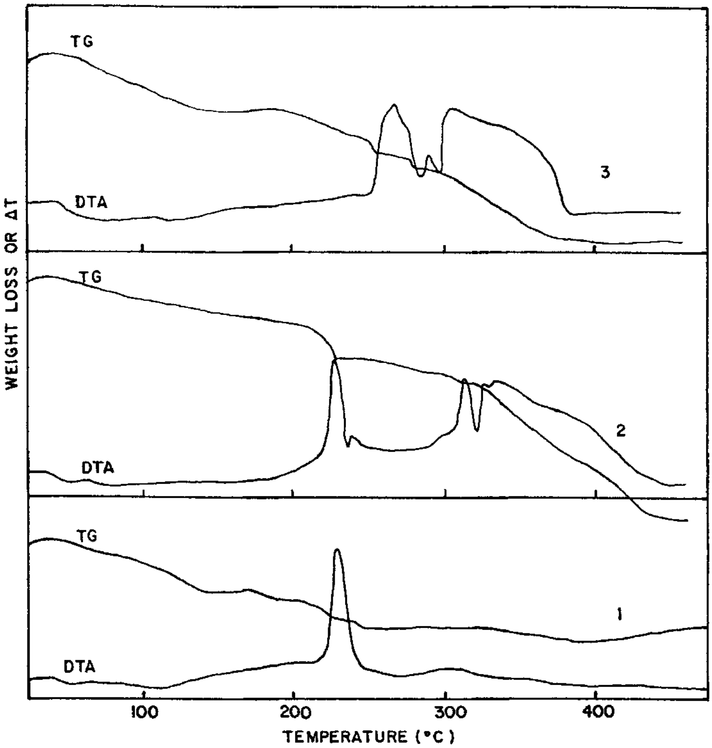

FIG. 6 TG and DTA curves of (1) copper hexacyanoferrate(II), (2) RCF, and (3) RCuCF-I. Temperature range: 20–500°C. Heating rate: 5°C/min. Sample weight: 20 mg.

thought of as

$$K_2CuFe(CN)_6{\cdot}2H_2O \rightarrow K_2CO_3 + {}^1\!/_2Fe_2O_3 + CuO$$

The calculated weight loss was 23.6% as against the observed weight loss of 25.5%. The minor discrepency in the calculated and observed weight loss may be due to the uncertain composition of copper hexacyanoferrate(II) $[K_{2x}Cu_{2-x}Fe(CN)_6]$. Similar exothermic peaks were observed in the cyanoferrate(II) form of Indion-810 resin (Fig. 6, Curve 2) at the same temperature of 230°C. However, thermograms of RCuCF-I (Fig. 6, Curve 3) showed that the decomposition of loaded copper hexacyanoferrate(II) resin takes place at the much higher temperature of 265°C, indicating an enhanced stability provided to the loaded salt which could only be due to the linking of copper hexacyanoferrate(II) to the quaternary

TABLE 3
Removal of ^{137}Cs from Spent Fuel Storage Pond Water by Copper-Hexacyanoferrate(II)-Loaded Resin[a]

Flow rate (BV/h)	Bed volumes passed	^{137}Cs in effluents (kBq/L)
10	200	6.29×10^{-3}
20	620	4.44×10^{-3}
30	1,090	3.70×10^{-3}
60	3,200	3.70×10^{-3}
40	4,000	7.77×10^{-3}
80	20,000	3.70×10^{-3}
80	30,000	5.92
80	49,000	16.65

[a]	
Resin	RCuCF-I
Particle size	0.3–1.2 mm
Bed volume	6.5 L
Flow rate	10 to 80 BV/h
^{137}Cs in feed	16.65 kBq/L

amine part of the anion exchanger. Thus the x-ray, IR, and thermal studies indicate that the loaded resin can be thought of as a chelate compound formed by the interaction of Cu^{2+}, $Fe(CN)_6^{4-}$, and the R_4N^+ group of the resin.

In order to demonstrate their usefulness in large-scale operations, a 6.5-L bed column was operated for polishing spent fuel storage pool water (20) in which cesium-137 is the major contaminant. The results are presented in Table 3 and show that copper hexacyanoferrate(II)-loaded resin is extremely efficient in removing radiocesium from pond water where it consistently reduces cesium activity in the pool from kBq/L to a few Bq/L.

CONCLUSIONS

Copper hexacyanoferrate(II)-loaded ion-exchange resins were prepared by using locally available macroreticular anion-exchange resins. These resins are highly selective for cesium from various salt and acid solutions. The resins also possess satisfactory column characteristics and therefore can be employed in large-scale operations for the removal of cesium from low level waste solutions. X-ray, infrared, and thermal studies indicated the formation of a chelate compound inside the resin matrix due to the interaction of copper hexacyanoferrate(II) with the amine part of the exchanger.

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