



A STUDY OF THE PROPERTIES OF HEXACYANOFERRATE SORBENTS AND THEIR USE FOR SORPTION OF CAESIUM AND STRONTIUM

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Abstract

A method of deposition of zinc, copper, and nickel hexacyanoferrates on silica-containing substrate (clinoptilolite) has been developed to produce mechanically strong sorbents for cesium and strontium separation from solutions of different compositions. The modification of clinoptilolite increases its sorption capacity for both cesium and strontium. Sorption behaviour of radionuclides was studied both in static and kinetic conditions.

1. INTRODUCTION

For the final removal of the long-lived radionuclides ^{137}Cs and ^{90}Sr in processes connected with the treatment of radioactive wastes and operation of nuclear power plants it is often recommended to use sorption columns with inorganic sorbents. We investigated some types of hexacyanoferrate sorbents to purify the aqueous wastes from cesium and strontium.

Nickel hexacyanoferrates are known to be effective sorbents of cesium [1-4]. This is accounted for by the stabilizing effect of large cesium ions on the structure of nickel hexacyanoferrates and by a resulting decrease in solubility of the product.

Our study is concerned with the effect of the chemical composition of nickel hexacyanoferrates, their solubility and their tendency to peptization on the sorption of cesium microquantities. Since the exchange of cesium for alkali metal ions in nickel hexacyanoferrates occurs more readily than that for nickel ions, the nature and content of the alkali metal in the hexacyanoferrate composition may have an appreciable effect on cesium sorption. Therefore, nickel hexacyanoferrates of various composition were prepared and investigated.

2. EXPERIMENTAL RESULTS AND DISCUSSION

Nickel hexacyanoferrates were produced by mixing the solutions: 0.1 M $\text{Ni}(\text{NO}_3)_2$ (A) and 0.1 M $\text{Na}_4\text{Fe}(\text{CN})_6$ (B1), or 0.1 M $\text{K}_4\text{Fe}(\text{CN})_6$ (B2), or 1.6 M NH_4NO_3 (B3), or 0.1 M $\text{Na}_4\text{Fe}(\text{CN})_6$, 0.2 M CsNO_3 (B4). Table I gives the volume ratios of the solutions and the order in which they were mixed and also the literature references to the conditions of preparation. In experiment 8 the product was labelled with ^{137}Cs . The composition of the products was determined by chemical analyses for nickel [9] and ferrocyanide [10], as well as radiometric analysis for ^{137}Cs in solutions before and after precipitation. A direct analysis of the compounds obtained was also made after their decomposition by a mixture of sulphuric and nitric acids. The concentrations of nickel and iron ions in the solution were determined using an AS-503 atomic absorption spectrometer.

The air-dried compounds were investigated using the X-ray powder diffraction technique on an ADP-10 diffractometer with CuK_α -radiation. The solubility of the compounds was

determined by analysis for nickel ions in the solution after equilibration using a Plasma-40 spectrophotometer (the method of emission spectroscopy with ICP- inductively coupled plasma). When determining the solubility of nickel, the release of Cs from the sample containing ^{137}Cs was also determined radiometrically.

In batch equilibration experiments, the sorbents (0.01 g) were mixed by shaking for 20 days (with night breaks) with 500 mL of the 0.1 M solution of sodium nitrate containing $4 \cdot 10^4$ Bq/L of ^{137}Cs . After equilibration the solutions were centrifuged and an aliquot of the supernatant was gamma-counted using a NaI(Tl) crystal detector at a NRG-603 gamma-automate facility (Tesla).

TABLE I. CONDITIONS OF PREPARING NICKEL FERROCYANIDES

N	Order of mixing	$\text{Ni}^{2+}:\text{Fe}(\text{CN})_6^{4-}$	Conditions of preparation
1	B_1 added to A	10:1	[5]
2	A to B_1	1.5:1	[6]
3	A to B_1	0.1:1	[5]
4	A to B_2	1.33:1	[3]
5	A to B_2	0.1:1	-
6	A to B_3	1.33:1	[7]
7	A to B_3	0.1:1	-
8	A to B_4	1:1	[8]

The compositions of the compounds obtained under the conditions given in Table I corresponded to those listed in Table II. The content of water in them was not determined, because it could hardly affect their sorption properties.

The composition of products of mixed nickel hexacyanoferrates for one and the same alkali metal ion depends on the ratio of the reagents being mixed, and the tendency of alkali metals to enter into the residue composition increases with the radius of their ions.

$\text{Na}_2\text{NiFe}(\text{CN})_6$ is only formed at the ratio $\text{Ni}^{2+}:\text{Fe}(\text{CN})_6^{4-} = 0.1:1$, while $\text{Cs}_2\text{NiFe}(\text{CN})_6$ is already formed at a ratio of 1:1.

The X-ray diffraction pattern of all the compounds prepared confirmed the earlier conclusion, that nickel, sodium and nickel, potassium hexacyanoferrates formed one isostructural group. Small differences in the X-ray diffraction patterns of these compounds are only observed in the values of relative band intensities (Fig. 1).

TABLE II. COMPOSITIONS OF NICKEL HEXACYANOFERRATES PREPARED.

N	Ni ²⁺ :Fe(CN) ₆ in the product	Compound	Colour of the residue
1	1.95	Ni ₂ Fe(CN) ₆	brownish green
2	1.48	Na ₂ Ni ₃ [Fe(CN) ₆] ₂	grass green
3	1.00	Na ₂ NiFe(CN) ₆	--"---
4	1.32	K ₄ Ni ₄ [Fe(CN) ₆] ₃	greenish blue light
5	1.00	K ₂ NiFe(CN) ₆	--"---
6	1.30	(NH ₄) ₄ Ni ₄ [Fe(CN) ₆] ₃	greenish blue
7	1.00	(NH ₄) ₂ NiFe(CN) ₆	blue
8	1.00	Cs ₂ NiFe(CN) ₆	light green

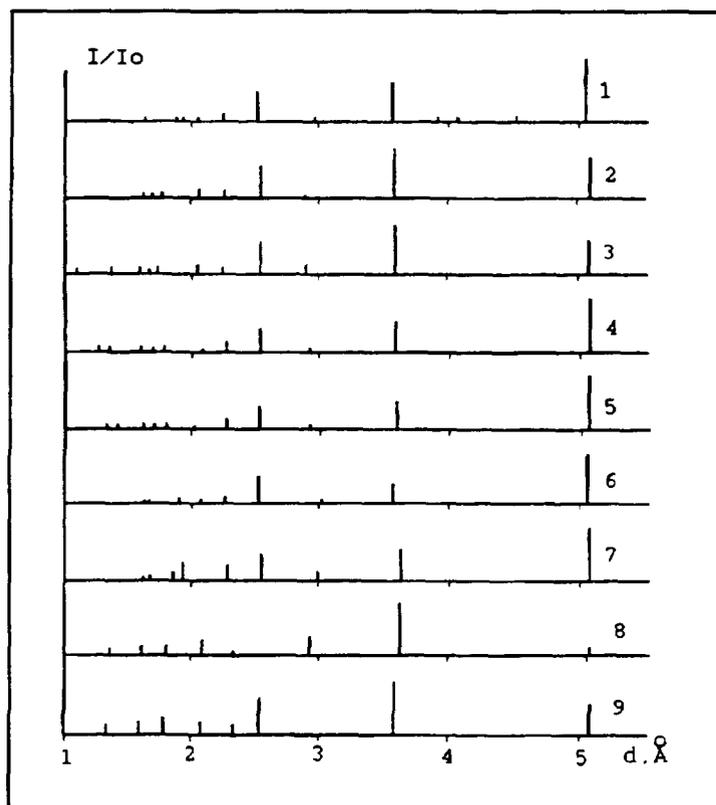


Fig. 1. X-ray diffraction patterns of nickel hexacyanoferrates:
 1-Ni₂Fe(CN)₆; 2-K₄Ni₄[Fe(CN)₆]₃; 3-K₂NiFe(CN)₆; 4-(NH₄)₄Ni₄[Fe(CN)₆]₃;
 5-(NH₄)₂NiFe(CN)₆; 6-Na₂Ni₃[Fe(CN)₆]₂; 7-Na₂NiFe(CN)₆;
 8-Cs₂NiFe(CN)₆; 9-sorbent.

Determining the solubility of nickel hexacyanoferrates presents certain difficulties that are related not only to their very low solubility but also to their tendency to peptization, particularly for compounds of the composition $\text{Me}_2\text{NiFe}(\text{CN})_6$, and transition to the solution of the colloidal form of the material.

In this work the solubility of the product was determined under the conditions excluding the penetration of the colloidal form of the residue (Table III). The residue, sealed in a dialysis film, was placed into a test tube with distilled water, stirred and changed after each five days. Equilibration was determined by the constant concentration of nickel ions in water. The experiments were conducted at 20°C.

TABLE III. SOLUBILITY OF NICKEL HEXACYANOFERRATES

Compound	Equilibrium concentration of Ni^{2+} , mg/L	Solubility, mol/L
$\text{Ni}_2\text{Fe}(\text{CN})_6$	0.080+/- 0.006	$7.0 \cdot 10^{-7}$
$\text{Na}_2\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$	0.079+/- 0.005	$4.5 \cdot 10^{-7}$
$\text{Na}_2\text{NiFe}(\text{CN})_6$	0.041+/- 0.006	$7.0 \cdot 10^{-7}$
$\text{K}_4\text{Ni}_4[\text{Fe}(\text{CN})_6]_3$	0.023+/- 0.003	$1.0 \cdot 10^{-7}$
$\text{K}_2\text{NiFe}(\text{CN})_6$	0.026+/- 0.003	$4.5 \cdot 10^{-7}$
$(\text{NH}_4)_4\text{Ni}_4[\text{Fe}(\text{CN})_6]_3$	0.016+/- 0.002	$7.0 \cdot 10^{-8}$
$(\text{NH}_4)_2\text{NiFe}(\text{CN})_6$	0.012+/- 0.002	$2.0 \cdot 10^{-7}$
$\text{Cs}_2\text{NiFe}(\text{CN})_6$	0.001+/- 0.0003	$2.0 \cdot 10^{-8}$

The values obtained show that the solubility of nickel hexacyanoferrates is very low. The higher literature values for $\text{Ni}_2\text{Fe}(\text{CN})_6$ - $2.6 \cdot 10^{-5}$ mol/L [12] are probably due to the presence in the solution of the colloidal form of the solid. As the radius of the monovalent ion increases from sodium to cesium, the solubility of the mixed nickel hexacyanoferrates decreases. The lowest value was obtained for $\text{Cs}_2\text{NiFe}(\text{CN})_6$ - $2.0 \cdot 10^{-8}$ mol/L.

The value of the ^{137}Cs distribution coefficient (K_d , mL/g) was determined in a 0.1 M solution of sodium nitrate labelled with ^{137}Cs . This composition of the solution was chosen to prevent possible peptization of the residues and to exclude its effect on K_d (Table IV).

The measurements showed that there was no correlation between the solubility of compounds and their sorption behaviour. Obviously, not only the solubility of the compounds but also the nature and the content in the compound of monovalent ions competing with cesium affect cesium sorption. Therefore, the highest K_d values were obtained for mixed nickel, sodium hexacyanoferrates.

During cesium adsorption from solutions containing compounds that attack the sorbent (alkalis, carbonates, phosphates, oxalates and the like) the solubility of the sorbents determines

TABLE IV. ¹³⁷Cs DISTRIBUTION COEFFICIENTS OF NICKEL HEXACYANOFERRATES

Compound	Kd,mL/g
Ni ₂ Fe(CN) ₆	1.4·10 ⁷
Na ₂ Ni ₃ [Fe(CN) ₆] ₂	2.6·10 ⁷
Na ₂ NiFe(CN) ₆	2.6·10 ⁷
K ₄ Ni ₄ [Fe(CN) ₆] ₃	1.0·10 ⁷
K ₂ NiFe(CN) ₆	0.2·10 ⁷
(NH ₄) ₄ Ni ₄ [Fe(CN) ₆] ₃	1.3·10 ⁷
(NH ₄) ₂ NiFe(CN) ₆	0.3·10 ⁷

their stability and Kd values. Therefore, to prepare cesium selective inorganic sorbents stable in salt solutions of complex composition, the least soluble nickel, ammonium and nickel, potassium hexacyanoferrates were chosen. The sorbent obtained by depositing these residues on silica gel contained 25 mg/g of nickel and 70 mg/g of hexacyanoferrates. ¹³⁷Cs Kds on this sorbent are rather high and equal to 2-3·10⁵ mL/g even at the Na₂CO₃ or H₂C₂O₄ concentration to 2 g/L.

The 0.1 M sodium nitrate labelled with ¹³⁷Cs (4·10⁴ Bq/L) was passed through the sorbent placed in a column to a depth of 10 cm at a flow rate of 0.025 cm/s. The volume of the purified solution was 30000 times as much as the sorbent volume, and the decontamination factor was 1000.

We investigated also the sorption on clinoptilolite modified by hexacyanoferrates. The final selection of sorbents is made according to the results of experiments under dynamic conditions. These experiments normally take a long time and complicate a comprehensive study of the sorption process. In this work, the possibility of a faster assessment of the properties of inorganic sorbents was studied. This assessment is based on a study of the initial regions of sorption yield curves at high solution flow rates and on establishing the dependence of the time of operation of the column, before the breakthrough of radionuclides, on the solution flow rate.

Extensive information is available from the literature on the use of sorbents prepared on the basis of transition-metal hexacyanoferrates (MeCF) for the extraction of ¹³⁷Cs [13-16]. For the extraction of ⁹⁰Sr, a natural zeolite-clinoptilolite (CP) is recommended [17, 18]. Methods of depositing hexacyanoferrates on CP were also proposed [19-21]. We developed our own method of depositing MeCF on a silicon-containing carrier. This method allows mechanically strong sorbents to be produced. Depending on the porosity of the carrier, these sorbents may contain from 3 to 50 wt % MeCF. We used this method for the deposition of zinc, copper, and nickel hexacyanoferrate precipitates on clinoptilolite (Dzegvi deposit, Georgia) particles. The resulting sorbents are listed in Table V.

The sorption properties of the prepared sorbents were studied in mains water of the following composition (mg/L): Na⁺, 6.4; K⁺, 3.9; Mg²⁺, 10; Ca²⁺, 42; Cl⁻, 4.6; SO₄²⁻, 48; HCO₃⁻, 157.

TABLE V. PARAMETERS OF THE MODIFIED CLINOPTILOLITE

Sorbent	Concentration in sorbent, mg/g		Bulk density, g/cm ³	Particle size, nm
	Me	Fe(CN) ₆		
ZFCP	13.2	32	1.1	0.25-0.50
NFCP	9.0	26	1.1	0.25-0.50
CFCP	10.5	20	1.1	0.25-0.50

Note: ZFCP, NFCP, and CFCP are sorbents prepared by the deposition of zinc, nickel, and copper hexacyanoferrates, respectively.

Radioactive tracers (either ¹³⁷Cs or ⁹⁰Sr) were added to the water up to a specific activity between 3.7 and 37 KBq/L. The liquid-solid phase ratio during the determination of the distribution ratios (DR) was 10000 for ¹³⁷Cs and 500 for ⁸⁵Sr. The time of stirring was 5 days. In addition, the cesium and strontium distribution ratios in water with an increased Ca²⁺ concentration (400 mg/L) were determined (Table VI).

TABLE VI. ¹³⁷Cs AND ⁹⁰Sr DISTRIBUTION RATIOS ON MEFCP-TYPE SORBENTS

Sorbent	Main water, 40 mg/L Ca ²⁺		Main water, 400 mg/L Ca ²⁺	
	DR ¹³⁷ Cs	DR ⁸⁵ Sr	DR ¹³⁷ Cs	DR ⁸⁵ Sr
CP	1.8·10 ⁴	0.7·10 ³	6.0·10 ⁴	2.0·10 ²
ZFCP	1.8·10 ⁵	2.7·10 ³	2.0·10 ⁵	7.0·10 ²
NFCP	2.5·10 ⁵	1.1·10 ³	2.2·10 ⁵	3.2·10 ²
MFCP	2.6·10 ⁵	0.7·10 ³	3.3·10 ⁵	2.2·10 ²

The modification of clinoptilolite with MeCF precipitates increases the affinity of clinoptilolite not only for cesium, but in some cases, for strontium, especially for the ZFCP sorbent. To determine the reason for the increase in the ⁸⁵Sr distribution ratio on ZFCP, we studied the ⁸⁵Sr distribution ratio on clinoptilolite in the zinc form [the sample was prepared by the treatment of clinoptilolite with a solution of Zn(NO₃)₂ (1 mol/L)], as well as on Zn₂Fe(CN)₆ and Na₂Zn₃[Fe(CN)₆]₂. The distribution ratios obtained were equal to 7·10², 1.2·10² and 1.3·10³ respectively. Consequently, the precipitation of the mixed zinc-sodium salt on the clinoptilolite increases its affinity for strontium.

The cesium and strontium sorption under dynamic conditions was studied on the ZFCP sorbent. The sorbent (2 cm³) was placed in a column with a diameter of 0.7 cm, and the solution was passed through from bottom to top. The solution flow rate was varied from 400 to 1600 column volumes/h in experiments with ¹³⁷Cs and from 20 to 85 column volumes/h in experiments with ⁸⁵Sr. Figure 2 shows the initial regions of the ¹³⁷Cs sorption curves.

As shown in [23], the system of the sorption dynamics equations in the case of outside diffusion and a convex sorption isotherm, which is the case with the ¹³⁷Cs sorption on ZFCP, allows the yield curve to be represented as a straight line:

$$\ln Z = K_1 t + K_0 \quad (1) \text{ or } \ln A/A_0 = \beta(A/\alpha)\tau - \beta(h/\omega) - 1 \quad (2),$$

where **A** and **A**₀ are the specific activities at the inlet and outlet of the column, **α** is the specific activity of the sorbent, **ω** is the linear solution flow rate; cm/s; **h** is the height of the sorbent, cm; **τ** is the time; and **β** is the kinetic coefficient of the outside diffusion, s⁻¹.

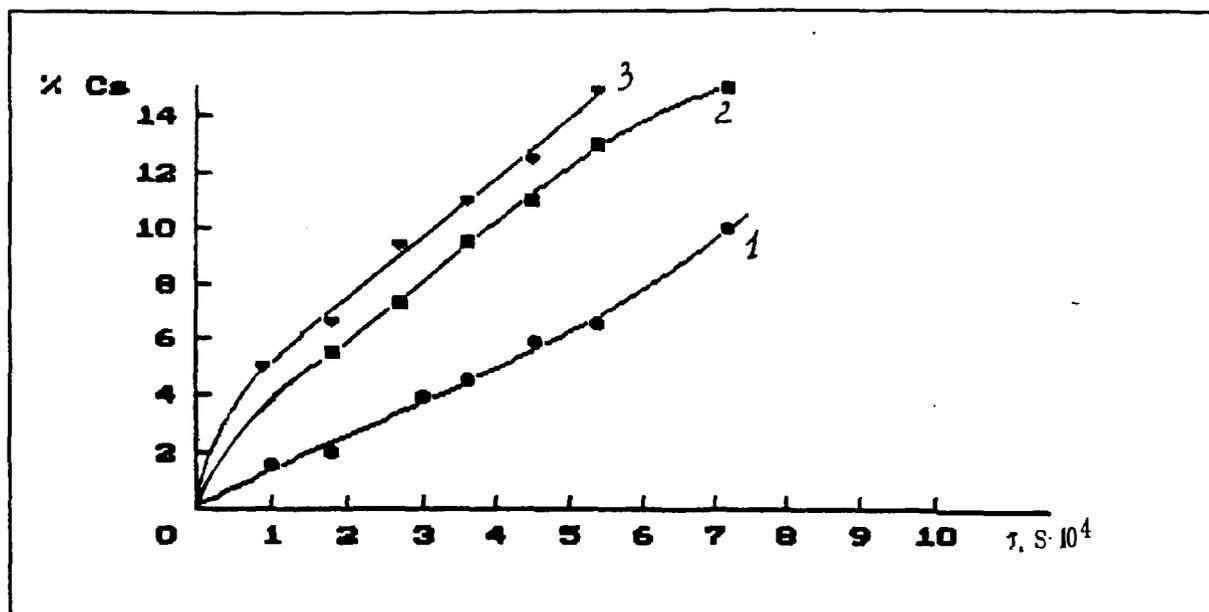


Fig. 2. The dependence of ¹³⁷Cs sorption on flow rate using ZFCP sorbent.
 1-400 column volumes/hour;
 2-826 column volumes/hour;
 3-1600 column volumes/hour.

The initial regions of the experimental yield curves for the ¹³⁷Cs sorption, calculated on the $\ln(A/A_0) = f(\tau)$ coordinates, are straight lines (Fig. 3).

This fact confirms the validity of using equation (2) for the description of this sorption process. From these data, the **K**₀ and **K**₁ coefficients in equation (1) were calculated using the least-squares technique. The kinetic coefficient of the outside-diffusion mass transfer was determined from **K**₀

$$\beta = (1 - K_0)\omega/h, \text{ (Table VII, Fig. 3)}$$

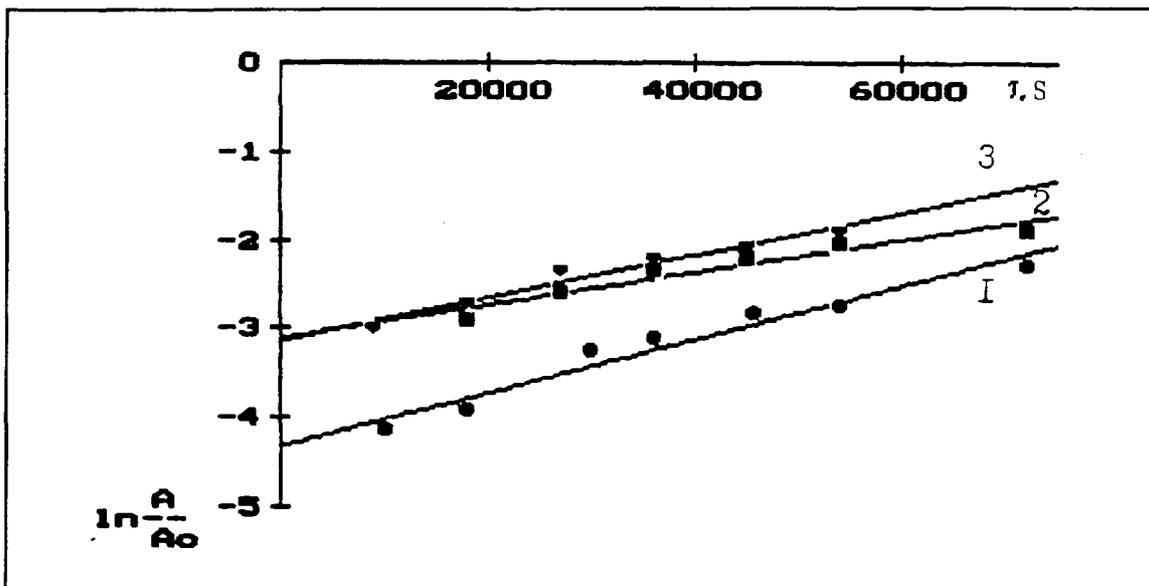


Fig. 3. The dependence of ^{137}Cs sorption on flow rate using ZFCP sorbent in the $\ln(A/A_0) = f(\tau)$ coordinates.

- 1-400 column volumes/hour;
- 2-826 column volumes/hour;
- 3-1600 column volumes/hour.

TABLE VII. DEPENDENCE OF THE KINETIC COEFFICIENT OF OUTSIDE DIFFUSION β ON THE SOLUTION FLOW RATE ω FOR ^{137}Cs SORPTION ON THE ZFCP SORBENT IN MAIN WATER

ω , cm/s	$\ln \omega$	β , s $^{-1}$	$\ln \beta$
0.203	-1.590	0.366	-0.999
0.419	-0.870	0.481	-0.723
0.811	-0.209	0.948	-0.053

The established dependence on the flow rate can be written as:

$$\ln \beta = 0.68 \ln \omega + 0.011.$$

The experiments on strontium sorption were carried out at a significantly lower flow rate because the rate of the ^{85}Sr sorption is significantly lower than that of ^{137}Cs . A comparison of the yield curves for sorption by ZFCP sorbents and nonmodified clinoptilolite in hard mains water (100 mg/L Ca^{2+}) confirmed the results obtained under equilibrium sorption conditions. Initial regions of three yield curves for ^{85}Sr sorption in mains water at different flow rates were obtained (Fig. 4).

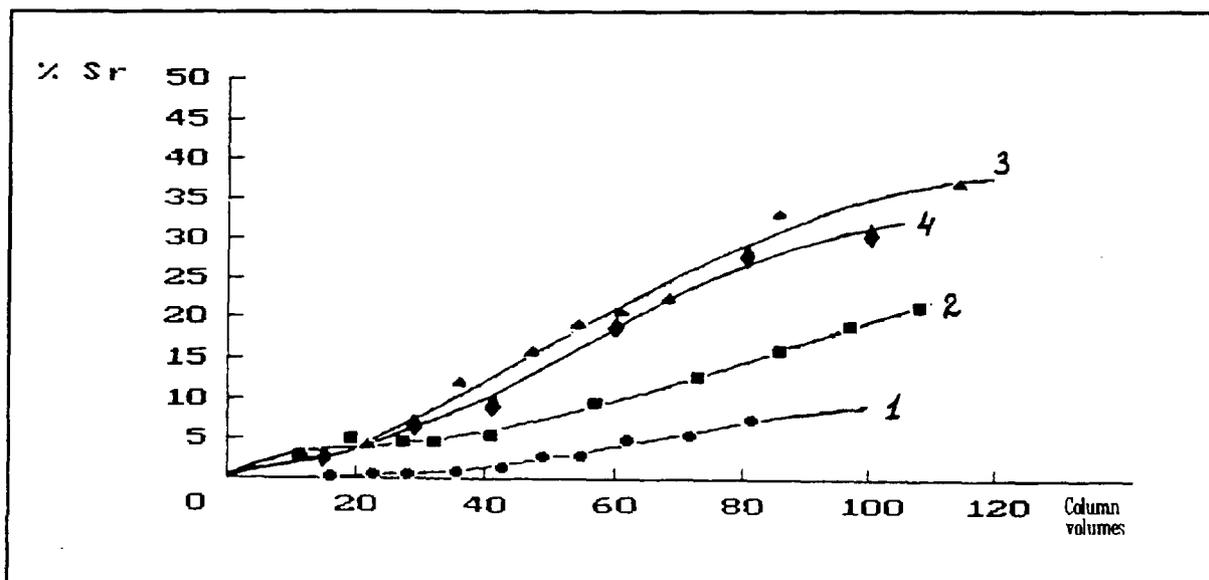


Fig.4. The dependence of the ^{85}Sr sorption on flow rate using ZFCP sorbent
 1-20 column volumes/hour;
 2-41 column volumes/hour;
 3-85 column volumes/hour.
 4-The dependence of ^{85}Sr sorption using clinoptilolite, flow rate - 20 column volumes/hour

On the $\ln A/A_0$ coordinates, these regions are also linear (Fig.5).

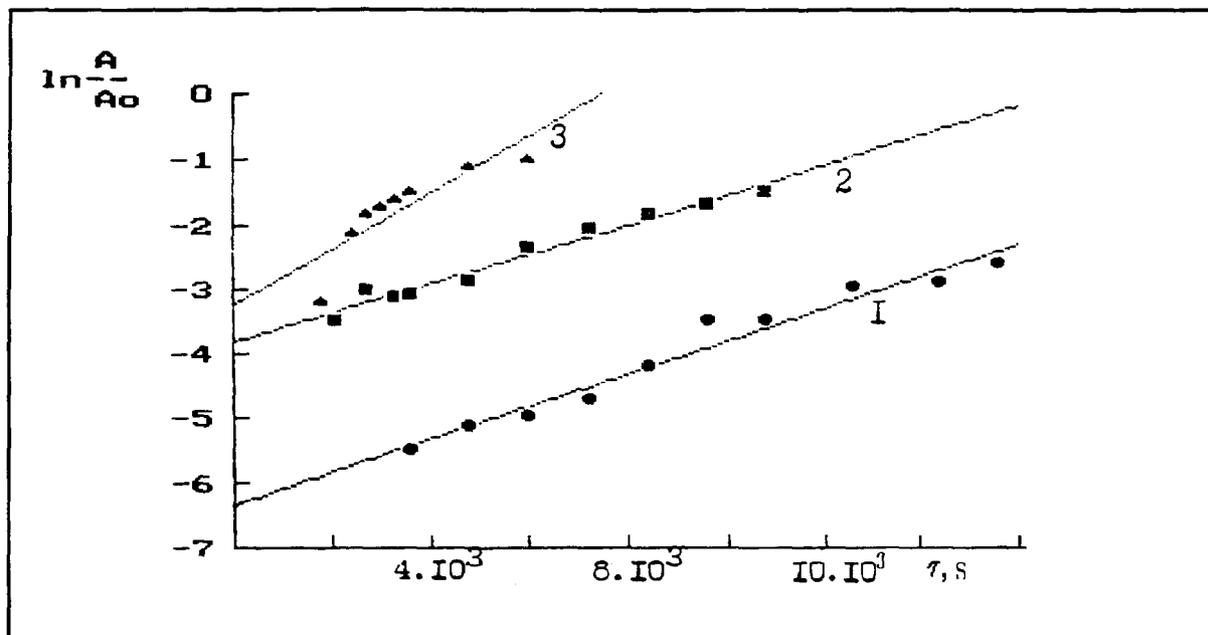


Fig.5. The dependence of ^{85}Sr sorption on flow rate using ZFCP sorbent in the $\ln(A/A_0) = f(\tau)$ coordinates.

1-20 column volumes/hour;
 2-41 column volumes/hour;
 3-85 column volumes/hour.

Nevertheless, attempts to fully linearize the yield curves for ^{85}Sr were unsuccessful. The outside diffusion is likely to be the limiting stage of the sorption process only at the initial moment of time. The dependence of the diffusion coefficients on the solution flow rate is described by the following equation

$$\ln\beta = 0.4 \ln \omega - 1.7.$$

Thus, the results obtained show that the ZFCP sorbent can be used for a simultaneous removal of ^{137}Cs and ^{90}Sr . In this process, the rate of solution flow through the sorbent is determined by the sorption of ^{90}Sr , which is a slower stage. The equations establishing the dependence of the β coefficients on the flow rate allow the calculation of the time of the protective effect of the column for selected flow rates.

CONCLUSIONS

- A method of the deposition of zinc, copper, and nickel hexacyanoferrates on a silica-containing substrate has been developed. This method allows mechanically strong sorbents to be produced. Depending on the substrate porosity, these sorbents may contain from 3 to 50 wt % MeCF.
- The modification of clinoptilolite increases its sorption capacity relative to both cesium and strontium.
- For selected flow rates (for cesium 100 - 3000 column volumes/hour; for strontium, 10 - 100 column volumes/hour), the extent of the protective action of the sorption column can be calculated from the experimental data according to the equation establishing the dependence of the coefficient b on the flow rate.

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