*Journal of Radioanalytical and Nuclear Chemistry, Vol. 242, No. 2 (1999) 387–390*

# Sorption of cesium on composite sorbents based on nickel ferrocyanide

**J. Orechovská, P. Rajec**

*Department of Nuclear Chemistry, Comenius University, 842 15 Bratislava, Slovakia*

(Received March 23, 1999)

Composite sorbents based on potassium nickel ferrocyanide embedded in silica gel matrix were prepared and characterised by powdered X-ray diffraction analysis, IR spectra, Mössbauer spectra and electron microscopy. The sorbent exhibits very good efficiency for cesium uptake and radiation resistance. The sorption capacity for cesium ions is comparable with the capacity for the pure ferrocyanides.

## Introduction

Inorganic sorbents are suitable for treating waste solutions to remove of harmful metals or radionuclides. The main advantages of inorganic sorbents are their high selectivity for some metals, radiation stability and compatibility with fixation processes, like cementation. On the other hand, compared with organic ones, they usually have lower capacities and their chemical stability is limited to narrower pH level. There are many types of inorganic sorbents used in the study of radionuclides and some of them have found technological application. Synthetic and natural zeolites, ammoniumphosphomolybdates (AMP) and ferrocyanides of transient metals, have been used for removal of cesium. Ferrocyanides (FCN) have been used for a long time and have been successfully applied in nuclear technology.[1,2] They possess high selectivity for the separation of cesium in the presence of alkaline and alkali metals, which enables them to be used for wastes with high salt contents. Another advantage of FCN is its high radiation and chemical stability in wide range of pH and low solubility. Usually, cesium sorption is done by exchange mechanism.

A large number of metals such as Ag, Zn, Cd, Cu(II), Ni, Co(II), Pb, Mn(II), Fe(III), Ti, Zr, V, Mo, W, U(VI) were used for the preparation of ferrocyanides.[3] Ferrocyanides are prepared by the precipitation method from aqueous solutions. Only a few ferrocyanides are prepared in a crystalline form suitable for application. More often, the precipitate is filtrated, dried and, after being crushing to small particles, the sorbent is put a sieve. In such a way $K_{1.76}Co_{1.12}Fe(CN)_6$ was prepared and used for the separation of $^{137}Cs$ from radioactive wastes of Loviisa NPP.[4] This product was stable enough to be used in a column. Separation of $^{137}Cs$ was very effective from wastes with a pH of 11.5. However, many ferrocyanides have the form of a fine powder and are not suitable for column application. To overcome this drawback, ferrocyanides are prepared by precipitation on a suitable support or are embedded in another matrix by preparing composite sorbents. Materials used as a matrix must fix ferrocyanides, must be chemically inert and must enable the preparation of composite sorbents with a high content of active sorbent.[5] Polyvinylacetate, polyvinylchlorid, polymethacrylate, polystyrene,[6] phenosulphonic resin,[7] acrylonitryle[8] were used as organic matrix materials. Silica gel was mainly used as a support for the precipitation of ferrocyanides,[9] also AMP was also embedded in silica gel.[10] A supported sorbent is not as suitable as one that is embedded. The matrix material influences sorption kinetics as well as reduces the surface supported by sorbent.

The aim of the work was to prepare and determine physico-chemical properties of a composite sorbent on a base of silica gel and potassium nickel ferrocyanides. By combining two different materials we could get a new type sorbent with the advantage of both of them. This means getting materials with the selectivity and sorption properties of ferrocyanides and with the mechanical parameters of silica gel.

## Experimental

### *Chemicals and preparation of sorbent*

All chemicals used were of pro analysis grade. Du Pond supplied $^{137}Cs$ tracer in the form of a solution in 0.01M HCl.

Potassium nickel ferrocyanides with different compositions were prepared from $K_4Fe(CN)_6$ or $Na_4Fe(CN)_6$ and $Ni(NO_3)_2 \cdot 6H_2O$. For the preparation of ferrocyanides embedded in silica gel matrix sol-gel method was used. The solutions of water glass, with different concentration of $K_4Fe(CN)_6$ or $Na_4Fe(CN)_6$, were mixed with an acidic solution of $Ni(NO_3)_2$. Precipitated solids dispersed in silica gel formed at the same time or a little later. After washing and drying the material we obtained sorbents with different composition. The composition of the prepared sorbents was determined after the decomposition of sorbents samples in boiling sulphuric acid. The amount of K, Ni and Fe in the solutions was determined by atomic absorption spectrometry (Perkin Elmer 1100).

*0236–5731/99/USD 17.00*

*Elsevier Science B. V., Amsterdam*
*Akadémiai Kiadó, Budapest*

### *Characterisation of sorbent*

Prepared sorbents were characterised by IR and Mössbauer spectroscopy, X-ray diffraction and electron scanning microscopy.

*IR spectroscopy:* Infrared spectroscopy measurements were performed on a Specord M-80 spectrometer (Germany). A few mg of the product were crushed, fixed with nujol oil and pressed between two CsI windows. The frequency range explored was between 400 to 4000 cm$^{-1}$.

*X-ray diffraction:* X-ray powder diffraction patterns were taken on a Philips diffractometer (CuK$\alpha$, $\lambda$=0.15405 nm) in the range 4–74° 2$\Theta$ at room temperature.

*Determination of the specific surface area:* The specific surface area of the sorbents was determined by using nitrogen absorption and the BET equation.

*Electron microscopic studies:* The morphology of the product was examined by using scanning electron microscope JXA-840A JEOL (Japan) operating at 15 keV.

*Mössbauer spectroscopy:* The Mössbauer spectra were performed on spectrometer NZ-640/2 (KFKI Budapest).

*Zeta potential:* Particle size distribution was determined by the dynamic light scattering technique, the angle being fixed at 90° (BI-90) and the electrophoretic mobility of the particles, from which the zeta potential was calculated. (Brookhaven Instruments Corporation).

### *Sorption experiments*

The sorption of cesium from aqueous solutions was investigated using a radiometric determination of the distribution coefficient, $K_d$ ($K_d=(a_0/a-1)\cdot(V/m)$, where $a_0$ and $a$ are volume activities of solution before and after interaction with the sorbent, respectively). The effect of potassium, sodium and calcium on cesium sorption behavior was studied in range $1\cdot10^{-2}$–$5\cdot10^{-6}$M, after adjustment to constant $1\cdot10^{-4}$M concentration of cesium. For each experiment 0.05 g of the materials was shaken for 2 hours with 5 ml of the aqueous solution in glass ampoules of 10 ml volume (12 mm inner diameter). The activity of $^{137}$Cs of 1ml of the individual solutions was measured by a gamma-spectrometer (Modumatic III, Packard, USA) after centrifugation at 12,000 rpm for 5 minutes.

The breakthrough curves were acquired by passing 0.02 res. 0.004M CsCl solution through exchanger columns with a diameter of 4 mm; the bed volume was 1 ml and the elution rate 24 bed volumes per hour.

## Results and discussion

### *Composition and structure of sorbents*

Composite sorbents with different amount of the active components have been prepared and the composition of selected sorbents is presented in Table 1.

Particle size of mixed nickel ferrocyanide synthesised by precipitation is relatively low and the obtained X-ray diffraction patterns show broad diffraction lines. In all cases the parameter $a_0$ close to 1 nm was found, which is in agreement with the data reported in the literature.[11] All infrared spectra show a sharp absorption band in the 2095–2100 cm$^{-1}$, which is characteristic for the $[Fe(CN)_6]^{4-}$ ion.[12] The strong absorption band in the 1100 region can be attributed to Si-O vibration.

Electron scanning microscopy was used to investigate the morphology of the sorbents, but with magnification up to 30,000 we could not find the crystals of ferrocyanide. Transmission electron microscopy would be probably more effective, but the preparation of the samples of the sorbent samples is complicated in this case. Mössbauer spectroscopy was used for determining of state of iron oxidation in the prepared sorbents. In sample IX the presence of Fe(III), caused by oxidation of Fe(II) in the preparation of the sample, was found. The integral of Mössbauer peak dependence on the amount of Fe in the composite sorbents is linear (Fig. 1).

*Table 1.* Composition of the selected sorbents

| Sorbent | Composition |
|---|---|
| IV | $K_{1,48}Ni_{1,26}Fe(CN)_6\cdot 1,01\ KNO_3$ |
| VIII | $K_{1,62}Ni_{1,19}Fe(CN)_6$ |
| IX | $Ni_2Fe(CN)_6\cdot 2,93\ KNO_3$ |
| XI | $K_{1.38}Ni_{1.31}Fe(CN)_6\cdot 0,95\ KNO_3$ |

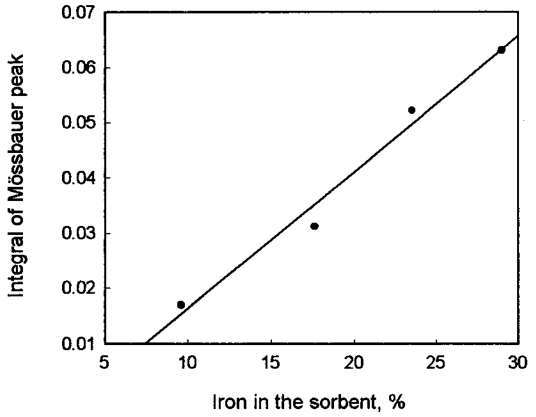

*Fig. 1.* Integral of Mössbauer peak vs. amount of Fe in composite sorbents

*Table 2.* Characterisation of the samples

| Sample | FCN by the preparation, % | Surface area, $m^2/g$ | Bulk density, ml/g |
|---|---|---|---|
| IV | 9.6 | 113 | 0.70 |
| VIII | 9.6 | 562 | 0.50 |
| IX | 17.6 | 504 | 1.00 |
| XI | 29.0 | 184 | 0.51 |

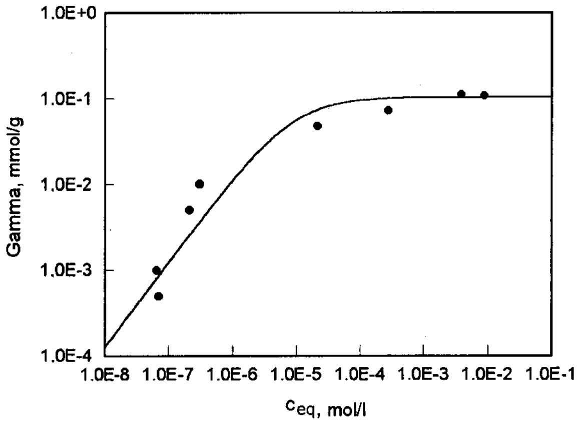

*Fig. 2.* Sorption isotherm of cesium on sorbent VIII

Some of the composite sorbents characteristics are given in Table 2. The surface area does not depend on the amount of active component in the composite sorbent.

*Sorption experiments*

The sorption of cesium on hexacyanoferrate incorporated in silica gel matrix was studied in the concentration range $1\cdot10^{-1}$–$10^{-5}$M. The results of concentration dependence on adsorption were fitted by Langmuir equation. The maximum cesium uptake values are presented in Table 3 and the typical sorption isotherm is given in Fig. 2. The decrease of distribution coefficient below and above the concentration $1\cdot10^{-4}$M has been observed (Fig. 3). Decrease of the $K_d$ in the case of high concentration of cesium is due to a decrease of the sorption capacity by cesium occupying of sorption site of sorbents. But, decrease of the $K_d$ for very low concentration ($<1\cdot10^{-4}$M Cs) is typical for those sorption experiments where colloids are present in solutions. The colloids may be also formed by fine sorbents particles, as can be observed in the case of ferrocyanides. Thus, a maximum on the curve in Fig. 3 has been observed. It was proven that $K_d$ increased after the removal of colloids by ultrafiltration (cut off 20,000) by two order (from 1650 to $1.5\cdot10^5$). A particle sizer was used to investigate the formation of colloids. After removing the bigger particles by filtration through a 1 μm size filter, particles with an average size of 120 nm were determined in the solution. A Zeta potential of −13.46 mV indicates that the particles have negative charge.

According to the assumption that theoretical cesium capacity of ferrocyanide is 2 mol/mol ferrocyanide or 2*n* mol/mol ferrocyanide for $n<1$ in $A_{2n}M_{2-n}Fe(CN)_6$, obtained values of cesium capacity are relatively high considering that the amount of potassium nickel ferrocyanide is in range 9.6–29% and comparing with the maximum uptake reported in literature[1] for pure ferrocyanides. The effective cesium capacity was calculated from the 10% breakthrough from columns with various sorbents and given in Table 4. For the most of sorbents, value obtained corresponds with those we measured in the batch experiments.

*Effect of competitive ions*

The effect of $K^+$, $Na^+$ and $Ca^{2+}$ ions on the distribution coefficient of cesium on composite sorbent was investigated. The distribution coefficient of Cs as a function of competitive ions for sample VIII, is presented in Fig. 4. As can be seen, sodium ions have a negligible effect on the ion exchange of cesium ions. Potassium ions decrease the distribution coefficient at concentrations higher than $5\cdot10^{-3}$M.

*Table 3.* Capacity of some sorbents for cesium (in mmol/g)

| Sorbent | Estimation of capacity (isotherm) | Calculated capacity (Langmuir equation) |
|---|---|---|
| IV | 0.47 | 0.42 |
| VIII | 0.11 | 0.10 |
| X | 0.23 | 0.26 |
| XI | 0.56 | 0.50 |

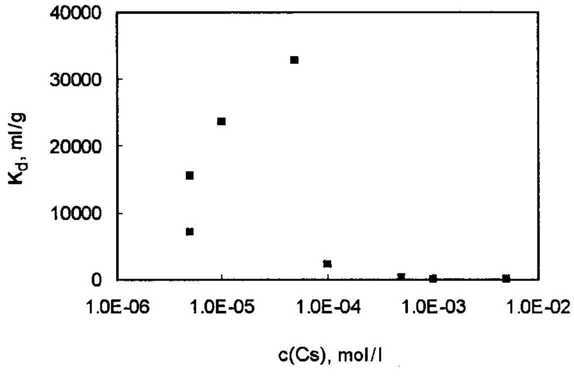

*Fig. 3.* Distribution coefficient of cesium as a function of concentration

*Table 4.* Cesium capacity for selected sorbents (in mmol/g) obtained by 10% breakthrough

| Sorbent | IV | VIII | X | XI |
|---|---|---|---|---|
| Capacity | 0.46 | 0.09 | 0.18 | 0.42 |

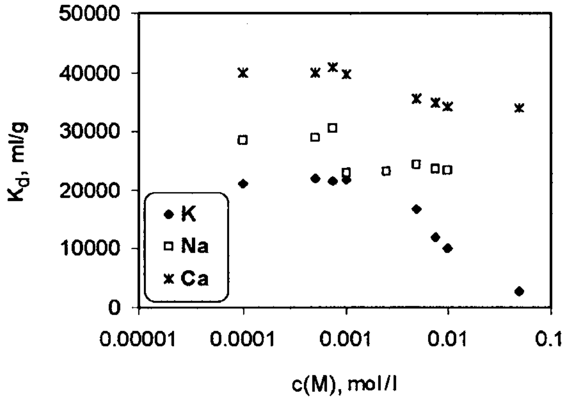

*Fig. 4.* Distribution coefficient of cesium as a function of competitive ions concentration

The competing influence of $K^+$ ions could be expected due to their similar ionic radius, similar hydration energy, dimension and charge density. In the presence of calcium ions, the distribution coefficient is higher than without competitive ions. This fact can be explained by coagulation effect of Ca ions on colloidal particles present in the solution due to their negative charge.

### *Radiation stability*

Radiation resistance of potassium nickel ferrocyanide in a silica gel matrix was studied by exposing samples to gamma-irradiation doses $1 \cdot 10^5$ Gy. The effect of irradiation on the ion exchange properties was examined by determining the uptake the cesium and the distribution coefficient of $^{137}$Cs before and after irradiation. The observed effect on sorption properties was none or negligible. The difference in the ion exchange capacity between nonirradiated and irradiated sorbent was 6%, which is within the tolerance of experimental error.

## Conclusion

The composite sorbent combines the high selectivity and capacity for cesium of potassium nickel ferrocyanide with the good mechanical stability of the silica gel binding matrix. This ion exchanger is suitable for continuous flow system for the removal of radiocesium from solutions with different amount of competitive ions.

*

The authors wish to acknowledge to Ing. Ivan NOVAK for the assistance in preparing of composite potassium nickel ferrocyanide sorbent and determining the specific surface area. Also, we wish to acknowledge to CLEOM laboratory, Comenius University for electron microscopy of samples, to Professor J. LIPKA of Electrofaculty of Slovak Technical University for measuring the Mössbauer spectroscopy, to E. SAMAJOVA of Comenius University for measuring the X-ray and to the Brookhaven Instruments Corporation for determining the Zeta potential and light scattering measurement.

## References

1. P. A. HAAS, Sep. Sci. Technol., 28 (1993) 2479.
2. J. LEHTO, R. HARJULA, E. TUSA, A. PAAVOLA, Proc. 1993 Intern. Conf. on Nuclear Waste Management and Environmental Remediation, Vol III, Prague, 1993, p. 763.
3. J. DOLEŽAL, V. KOUŘIM, Radiochem. Radioanal. Lett., 11 (1969) 351.
4. J. LEHTO, R. HARJULA, Proc. of Final Research Co-ordination Meeting, IAEA-TECDOC-675, Řež, 1991, p. 131.
5. F. ŠEBESTA, J. Radioanal. Nucl. Chem., 220 (1997) 77.
6. J. STEJSKAL, J. SOUKUP, J.DOLEŽAL, V. KOUŘIM, J. Radioanal. Nucl. Chem., 21 (1974) 371.
7. J. NARBUTT, A. BILEWICZ, B. BARTOŚ, Chem. Analityczna, 33 (1989) 399.
8. F. ŠEBESTA, Czech Patent PV 4523-88Q.
9. C. KONEČNÝ, R. CALETKA, J. Radioanal. Chem., 14 (1973) 255.
10. J. DOLEŽAL, J. STEJSKAL, M. TYMPL, V. KOUŘIM, J. Radioanal. Chem., 21 (1974) 381.
11. C. LOOS-NESKOVIC, M. FÉDOROFF, E. GANIER, Talanta, 36 (1989) 749.
12. C. LOOS-NESKOVIC, M. FÉDOROFF, Solvent Extr. Ion Exch., 7 (1989) 131.