Journal of Radioanalytical and Nuclear Chemistry, Vol. 237, Nos 1–2 (1998) 97–102

Preparation, characterization, and utilization of potassium nickel hexacyanoferrate for the separation of cesium and cobalt from contaminated waste water

I. M. Ismail,* M. R. El-Sourougy, N. Abdel Moneim,* H. F. Aly****

* *Cairo University, Chemical Engineering Department, Giza, Egypt*
** *Atomic Energy Authority, 101 Kaser El-Eini Street, Cairo, Egypt*

(Received February 16, 1998)

A method for the preparation of potassium nickel hexacyanoferrate complex $K_2NiFe(CN)_6 \cdot 3H_2O$ (KNiFC) with acceptable properties was developed. The complex was characterized by its solubility in different nitric acid media, thermal stability, IR spectrometry, X-ray diffraction, and scanning electron microscopy. Utilization of the prepared potassium nickel hexacyanoferrate as ion exchanger for the removal of cesium and cobalt from radiocontaminants on laboratory scale using fixed bed technique was studied.

Introduction

The separation of some relatively long-lived radioactive nuclides such as ^{137}Cs and ^{60}Co from waste water effluents is not quite effective owing to the low affinity of the conventional demineralizers for these ions. Moreover, organic resin beds are not radiation or high temperature resistant, and can not be directly immobilized into concrete for final disposal. Inorganic fixators, especially antimonates,[1,2] molybdophosphates,[3] and insoluble hexacyanoferrates seem to be promising for such purpose. Different ferrocyanide complexes had been used for such purpose such as ferri-ferrocyanide nickel,[4] copper ferrocyanide,[5] etc. Most of the materials obtained by classical precipitation are physically fragile and require a solid support when used in columns. Some authors mixed the hexacyanoferrates with silica as a neutral support to improve the mechanical strength of the product so it could be used as a resin for the fixed bed column. VLASSELAR et al.[6] filled the column with a mixture of zinc potassium hexacyanoferrate and silica at a weight ratio of 1:4. KONECNY et al.[7] prepared nickel or zinc hexacyanoferrate by precipitation of nickel or zinc salt with chromatographic silica gel impregnated by potassium hexacyanoferrate. Another approach was taken by WATARI et al.[8] where nickel hexacyanoferrate was prepared inside the cavities of a macroreticular anion exchanger resin. Repeated precipitation increased the nickel hexacyanoferrate content in the resin to 64%. These procedures dilute the sorbing material and therefore decrease its sorption capacity. MIMURA et al.[9] prepared a nonstoichiometric potassium nickel hexacyanoferrate, KNiFC for the purpose of selective removal of Cs. The chemical and thermal stability of the product as well as the distribution coefficient of Cs were studied.[9,10] They showed that potassium nickel hexacyanoferrate has the highest uptake of cesium among different inorganic ion exchangers. However, their product was not utilized for the solid bed technique. Accordingly, it is important to find a new preparation method in which we do not use any supporting material and having a product possessing high mechanical strength suitable for the solid bed operations.

Therefore, the present work was directed to develop a method for the preparation of potassium nickel hexacyanoferrate with high stability for the fixed bed utilization. The column performance of cesium and cobalt breakthrough was studied in terms of flow rate and the material balance of the systems.

Experimental

Preparation of potassium nickel hexacyanoferrate complex

Many preparation methods were reported for hexacyanoferrate complexes.[9,11–13] Most of these methods precipitated the complex by reacting $K_4Fe(CN)_6$ with Ni^{+2} salt. The resultant slurry was to be filtered, dried and ground. In this work the same principle was followed. The effect of ingredient ratio, pH, temperature, aging time, and the temperature of the drying air on the product solubility was studied. $NiSO_4$, $Ni(NO_3)_3$ and $NiCl_2$ were also used for the preparation of the complex. The developed method based on these preliminary studies is as follows.

A 0.094M $K_4Fe(CN)_6$ solution was added to 0.113M $NiSO_4$ at a volume ratio of 1:2, respectively, at ambient conditions. The slurry formed was aged over one week. Precipitation and aging were carried out at pH 5.5. The slurry formed was filtered under vacuum and dried at 45 °C for 24–48 hours, depending on the thickness of the filtered cake, using air dryer. The temperature of the air dryer was reduced gradually to the ambient temperature; then the product was ground and screened.

0236–5731/98/USD 17.00

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

Characterization of the prepared complex

The physicochemical properties of the prepared complex were investigated by different techniques as follows.

Solubility: To measure the effect of particle size on the solubility of the complex, 25 ml of distilled water at pH 5.5 was added to 0.1 g of the complex of different particle sizes, it was shaken for 2 hours at 800 vibration/min and then left for one week. The solution was filtered and analyzed for nickel and potassium using a 902 GBC atomic absorption spectrophotometer. To measure the effect of pH on the solubility of the complex, 0.025 g of complex was added to 25 ml of the solution at ambient conditions. The pH of the solution was adjusted by HNO_3. Then, the samples were shaken, left for one week, and filtered. The concentrations of Ni^{2+}, K^+, Fe^{3+} in the filtered solutions were measured as mentioned before.

Differential thermal analysis: The physical and chemical changes of the prepared complex, when subjected to heat, were examined. The sample was heated at a rate of 10 °C/min for 85 minutes starting from ambient conditions using a Shimadzu TGA-50 thermal analyzer.

IR spectroscopy: The IR spectra of the complex was measured using the disc technique. In this concern, every sample was thoroughly mixed with KBr as a matrix and the mixture was ground and then pressed with a special press to give a disc of standard diameter. The IR spectra of $K_4Fe(CN)_6$ which were used for the preparation of KNiFC, KNiFC complex, KNiFC loaded with cesium, KNiFC loaded with cobalt, and KNiFC heated up to 550 °C, were scanned over the wavelength range of 600–4000 cm^{-1}.

X-ray diffraction: The complex was fixed on a glass slide using a suitable binder. The X-ray was scanned from an angle from 4° to 80°. A copper anode tube (PW2272/20) was used with nickel filter during the scanning.

Scanning electron microscopy: The ground complex was compressed to give a pellet of suitable diameter. This was followed by washing it with chloroform. The pellet was dried for three days at 110 °C. Then it was gold-sputtered before examination.

Column technique

Solid-bed investigations were carried out using a column of 10 mm inner diameter and 100 mm length. The column was packed with 2 g of the complex having a particle size of 0.074–0.037 mm. The bed height and volume were 2.7 cm and 2.12 ml, respectively. This was followed by conditioning using an aqueous solution of pH 2. A solution of cesium or cobalt of initial concentration of 1000 mg/dl was passed through the column using a liquid pump. In case of simultaneous uptake of cesium and cobalt, a solution of both cesium and cobalt containing 1000 mg/dl of each was passed through the solid bed.

Results and discussion

The solubility of the prepared complex in different solutions of different hydrogen ion concentrations was determined in terms of nickel, potassium, and iron ion concentration at ambient conditions. Figure 1 shows the plot of solubility of each ion in g ion/100 ml solution versus the pH of the solution. From this figure it is clear that the amount of nickel, potassium, and iron dissolved generally increase with the increase of hydrogen ion concentration. In this concern $0.67\cdot10^{-2}$ g/100 ml of nickel was dissolved in a solution of pH 1.15 and only $0.4\cdot10^{-2}$ g/100 ml was found to dissolve in a solution of pH 5.7. In case of iron an amount of $0.01\cdot10^{-2}$ g/100 ml was found to dissolve in a solution of pH 1.15 and nearly nothing was dissolved in a solution of pH 5.7. The potassium solubility in a solution of pH 1.15 was reported to be $2.9\cdot10^{-2}$ g/100 ml and was decreased to a value of $1.2\cdot10^{-2}$ g/100 ml at pH 5.7. The ratio of K, Ni, and Fe dissolved in the solution is not the same as their ratio in the solid complex. The small amount of Fe dissolved in the solution represents the amount of complex dissolved by the complete dissociation of the amorphous KNiFC complex. The amounts of K and Ni found in solution are much higher than the stoichiometric amount related to the amount of Fe dissociated. It is believed that the excess over the stoichiometric amount was replaced by H^+ ions from the complex which exists in solution due to the ion exchange process. This is highly supported in case of K by the exponential relation between the pH and the amount of K released. The sorption of H^+ ions by the complex had to increase the pH of the solution, but as the amount of the solid used in this experiment was very small, the change in pH was below the sensitivity of the pH meter. To assess the H^+ ion exchange with K and Ni ions, 2 g of the complex was packed in a column and at pH 5.5 water was allowed to pass through the column. The pH increased to such a degree that $Ni(OH)_2$ precipitate was formed and the pressure drop over the column increased gradually till the flow finally stopped. Adding a small droplet of HNO_3 to the top of the column, the $Ni(OH)_2$ dissolved and constant flow was resumed. This test assured that H^+ ions were sorbed by the complex replacing Ni and K ions giving chance pH to increase the pH of the solution. So, the major part of the K and Ni amounts released to the solution are not physically dissolved and the physically dissolved amounts are rather limited. In case of presence of Cs and/or Co ions in the solution, they are sorbed by the complex instead of H^+ ions. The effect of pH on the Cs sorption is discussed elsewhere.[14] The effect of particle size on the solubility of the complex was determined based on the solubility of nickel ions. The obtained results showed that the particle size has no effect on the solubility of the complex. From these results, it can be concluded that increasing the pH of the solution the solubility of the complex decreases in the range of 1–6, irrespective of the particle size.

The thermal stability of the prepared complex was measured using thermal gravimetry (TG) and differential thermal analysis (DTA) techniques. Figure 2 shows the obtained chart. From this chart, the amounts of released water at different temperatures were calculated. In this concern, the prepared complex was assumed to have the molecular formula $K_2NiFe(CN)_6{\cdot}xH_2O$. The percent loss in weight from 80 to 90 °C was found to be 4%, which corresponds to the release of some fraction of water. This water could be the moisture water of the complex. By further heating up to 180 °C, a loss in weight of about 12% occurred, which corresponds to the release of 3 molecules of water. This water is probably related to the water of crystallization of the complex. Further increase in the temperature indicate that the complex is stable up to 350 °C when an exothermic peak is obtained indicating the dissociation of the complex and the breakage of the C≡N bond.

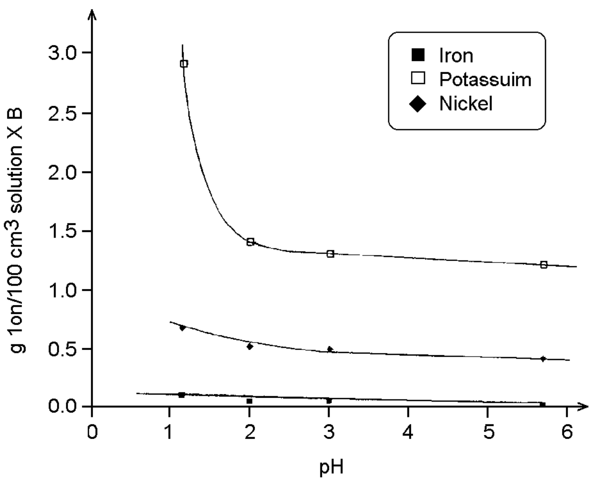


Fig. 1. Effect of pH on the solubility of KNiFC, B values are 1000 for iron, 100 for nickel, and 100 for potassium

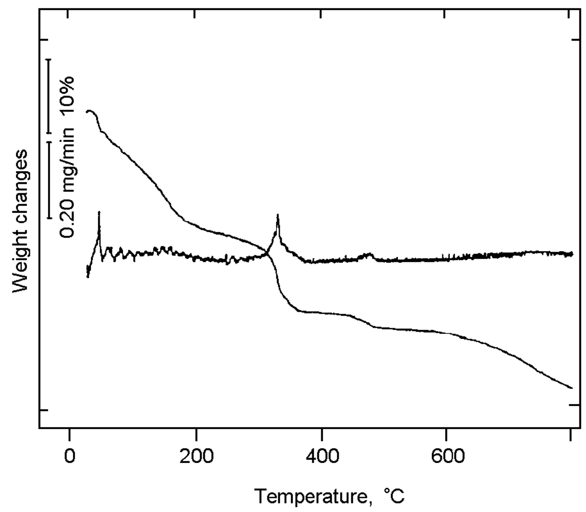


Fig. 2. Thermal analysis (TA and DTA) of KNiFC

The IR spectra of $K_4Fe(CN)_6$ used for preparation of KNiFC, that of KNiFC prepared, KNiFC loaded with cesium, KNiFC loaded with cobalt, and KNiFC heated up to 550 °C are given in Figs 3a, b, c ,d, and e, respectively. The IR spectra of $K_4Fe(CN)_6$ and KNiFC are characterized by the C≡N stretching band in the region 2000–2100 cm^{-1}. The absorption bands at 3000–3500 cm^{-1} and 1610 cm^{-1} are characteristic for H_2O stretching vibration and water in the crystal lattice of the compound, respectively. This spectra matches the spectra published by GELLINGS.[15] When cesium and cobalt were loaded on the KNiFC, the IR spectra obtained was changed. In the case of cesium loading, the C≡N band present at 2080 cm^{-1} in KNiFC was shifted to 2100 cm^{-1} together with a high decrease in the intensity of the band at 1100 cm^{-1}. In addition, a new band at 1385 cm^{-1} appeared indicating the presence of C-N bond. These changes indicate the strong bonding of cesium with KNiFC. On the other hand, the IR spectra of KNiFC loaded with cobalt showed no change for the C≡N band at 2080 cm^{-1}, a slight shift for the band in the region 1600–1610 cm^{-1} together with a high decrease in the intensity of the band at 1100 cm^{-1}. The IR spectra of KNiFC heated up to 550 °C indicated the disappearance of the C≡N band at 2100 cm^{-1} and that of the water stretching vibrations band at 3500 cm^{-1}. This supports the previous findings of the rupture of the C≡N bond at 350 °C as indicated by the TG and DTA results.

Table 1 shows the X-ray diffraction results obtained in the form of relative intensity (I/I_o) versus layer spacing (d) for KNiFC, KNiFC loaded with Cs, KNiFC loaded with Co, KNiFC loaded with Cs & Co and $K_2NiFe(CN)_6{\cdot}3H_2O$, respectively. Comparing the results of these different forms of KNiFC with the results obtained from the literature[15,16] for $K_2NiFe(CN)_6{\cdot}3H_2O$, it is clear that the complex peaks do not completely match with the published peaks of $K_2NiFe(CN)_6{\cdot}3H_2O$. One major peak, at $d=5.042$, as well as two smaller peaks had disappeared. From these results, it can be suggested that KNiFC is a semicrystalline complex. The peaks obtained after loading with cesium show that some changes occurred, two peaks had appeared and one peak had disappeared.

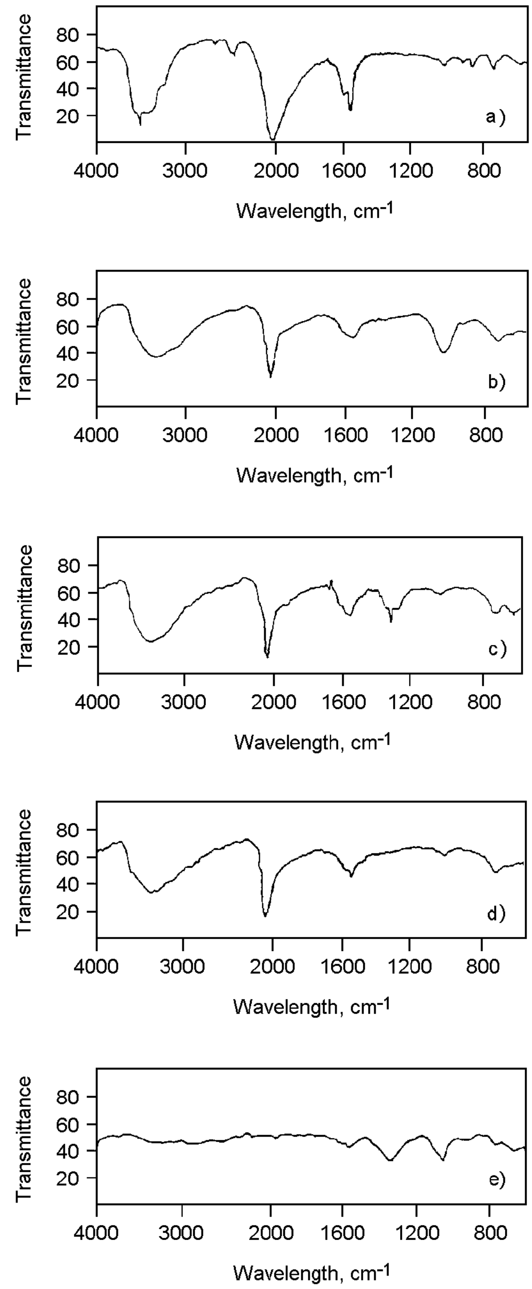


Fig. 3. The IR spectra of (a) $K_4Fe(CN)_6$, (b) KNiFC, (c) KNiFC loaded with cesium, (d) KNiFC loaded with cobalt, (e) KNiFC heated up to 550 °C

The pattern of the complex loaded with cesium shows the published pattern of $Cs_2NiFe(CN)_6$. This indicates that sorption of cesium is accompanied by structure changes. This was also supported by the IR spectra changes of KNiFC after loading with cesium. This could be the reason why it is usually difficult to regenerate the KNiFC after loading with cesium. It is believed that the most successful method for regeneration of ferrocyanide resins loaded with cesium is the electrochemical regeneration.[13] The loading of the complex with cobalt had slight changes on the relative intensity I/I_o of the peaks while the d values were the same. This means that the crystal structure is almost constant after and before the loading of cobalt. Loading the complex with both cesium and cobalt simultaneously had slightly shifted the d values obtained. Here also one peak had disappeared from the pattern. These findings indicate that loading of cesium affects the complex structure in a higher degree than does cobalt loading. The pattern obtained of a complex sample heated up to 550 °C at a rate of 10 °C/min, given in Table 2, is similar to that of Fe_3O_4 and NiO_2. These two oxides are expected to represent the final phase obtained after the breakage of the C≡N bond by heating the complex up to 550 °C.

Figure 4 shows the results obtained from the Scanning Electron Microscope and X-ray analysis, which indicate the presence of nickel, potassium, and iron. The peaks of nickel and iron were equivalent to each other, which support that the iron/nickel ratio is equal to 1.

Many attempts were carried out to dissolve the complex in any of the known mineral acids to identify its composition by chemical analysis. Unfortunately, the complex did not dissolve completely in any acid. Small solid residuals were observed in all cases. Analysis of the solution after filtration gives a ratio of K:Ni:Fe as 2:1:0.9. As the ratio of Ni:Fe was proved to be 1 from the SEM chart, it is believed that the solid residuals are iron compounds.

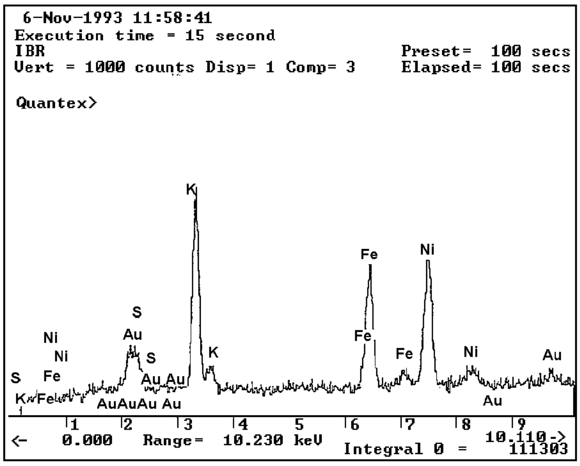
Based on the results obtained by TG, DTA, X-Ray diffraction, IR spectroscopy, and SEM, the following formula is suggested for the prepared KNiFC: $K_2NiFe(CN)_6{\cdot}3H_2O$. This formula matches that published in the literature.[15,17,18]

Fixed bed investigations: In Fig. 5 the results concerning the effect of the flow rate on the break-through of cesium are given. As shown in the figure, ideal break-through curves were obtained. Two flow rates of the feed solution were investigated. The break-through curves obtained indicate that using a flow rate of 1.56 cm^3/min, the cesium starts to break-through at the 148th bed volume and complete break-through is achieved at about the 273th bed volume. Calculation of the total amount of cesium sorbed showed that 312.5 mg cesium/g solid was sorbed. Comparing this value with the calculated equilibrium value,[14] the efficiency of the column using this flow rate is 30%. Decreasing the flow rate to 1.0 cm^3/min, the break-through started after the 184th bed volume and completely achieved after 230 bed volumes. In this case the total amount of cesium sorbed at break point was 390 mg/g solid and the efficiency of the column increased to 37.5%. This high capacity of KNiFC for cesium is almost twice of the capacity of ammonium molybdophosphate.[3]

Table 1. X-Ray data for various samples in the form of relative intensity I/I_o versus layer spacing d

KNiFC		KNiFC loaded with Cs		KNiFC loaded with Co		KNiFC loaded with Cs & Co		$K_2NiFe(CN)_6{\cdot}3H_2O$*	
I/I_o	d	I/I_o	d	I/I_o	d	I/I_o	d	I/I_o	d
								0.90	5.042
1	3.57	1	3.58	1	3.6	1	3.64	1.00	3.570
		0.238	2.93					0.10	2.900
0.8	2.54	0.714	2.55	0.91	2.54	0.76	2.56	0.64	2.54
0.286	2.262			0.52	2.26			0.15	2.24
0.36	2.055	0.428	2.08	0.41	2.06	0.4	2.1	0.15	2.06
0.27	1.79	0.38	1.79	0.44	1.79	0.44	1.8		
0.36	1.595	0.38	1.61	0.44	1.6	0.44	1.6		
		0.33	1.37						

* Reference 16.



```
 6-Nov-1993 11:58:41
Execution time = 15 second
IBR                                          Preset=  100 secs
Vert = 1000 counts Disp= 1 Comp= 3           Elapsed= 100 secs

Quantex>
<-    0.000   Range=  10.230 keV                      10.110->
                                      Integral 0 =     111303
```

Fig. 4. Scanning electron microscope (SEM) chart of KNiFC

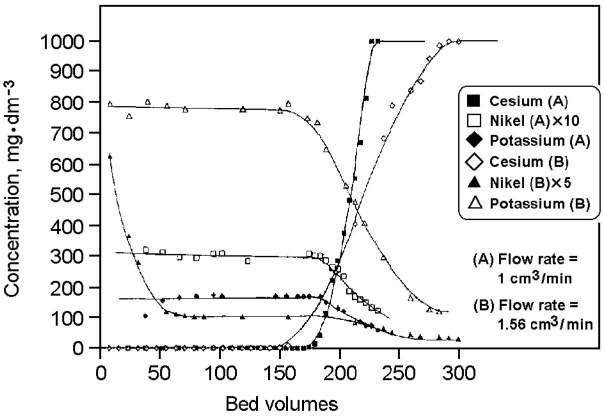


Fig. 5. Effect of the flow rate on the break-through curve of cesium

The break-through curve obtained in case of cobalt is shown in Fig. 6. It is clear that the break-through started at the first volume bed and the complete break-through was achieved after about 140 bed volumes. This means that the height of column used (2.7 cm) was less than the height of the sorption zone. Although the break-through is not the ideal one, it indicates that the complex is much more selective for cesium rather than cobalt.

In Fig. 7 the break-through curves in case of binary solutes (Cs and Co) are given. The break-through of cobalt started at the first bed volume and the complete break-through was achieved at the 47th bed volume. For cesium, the break-through started at the 57th bed volume and the complete break-through was achieved after 400 bed volumes. Such findings indicate that the cobalt uptake was retarded by the presence of cesium. Therefore, KNiFC could be used to separate cesium, to some extent, from solutions contaminated with cobalt ions.

To evaluate the mass balance of these systems, potassium and nickel ions were determined in the effluent solutions. In Figs 6, 7, and 8 the amount of potassium and nickel, eluted as a result of cesium and/or cobalt sorption, are given. The mass balance results show that the amount of sorbed cesium or cobalt is not equivalent to the amount released of potassium and nickel on mole basis. The percentage of uptake of cesium or cobalt by ion exchange mechanism was tentatively characterized by the following approximate formula (neglecting the physical solubility of the complex):

$$\%\ \text{uptake of cesium by ion exchange} = \frac{\text{Ni}^{2+}\cdot 2 + \text{K}^{+}}{\text{Cs}^{+}}$$

$$\%\ \text{uptake of cobalt by ion exchange} = \frac{\text{Ni}^{2+}\cdot 2 + \text{K}^{+}}{\text{Co}^{2+}\cdot 2}$$

where Ni^{2+} is the number of moles of nickel released, K^{+} is the number of moles of potassium released, Cs^{+} is the number of moles of cesium sorbed, and Co^{2+} is the number of moles of cobalt sorbed.

The value of the percent uptake of cesium by ion exchange mechanism, as defined above, was found to be 65% at a flow rate of 1.56 cm^3/min and 72% at a flow rate of 1 cm^3/min while for cobalt this value is only 27%. The remaining sorbed moles are believed to be sorbed by physical adsorption.

Table 2. X-ray data for KNiFC heated up to 550 °C in the form of relative intensity, I/I_o, versus layer spacing, d

I/I_o	d	Identified to
0.34	3.01	Fe_3O_4
0.319	2.9	Fe_3O_4
0.702	2.53	Fe_3O_4
0.49	2.43	NiO_2
1	2.09	NiO_2
0.617	2.055	NiO_2
0.276	1.77	NiO_2
0.383	1.61	Fe_3O_4
0.936	1.48	NiO_2
0.319	1.26	Fe_3O_4

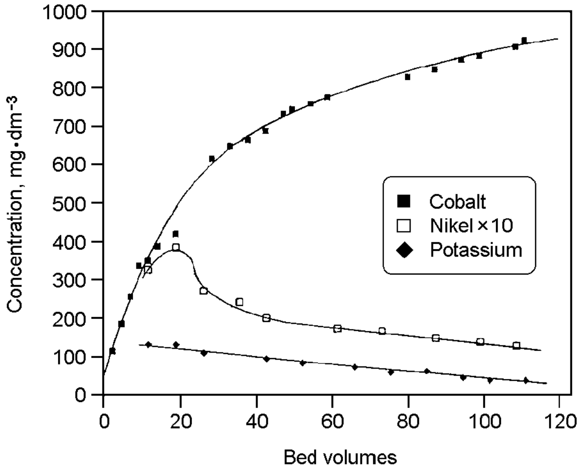


Fig. 6. Break-through curve of cobalt

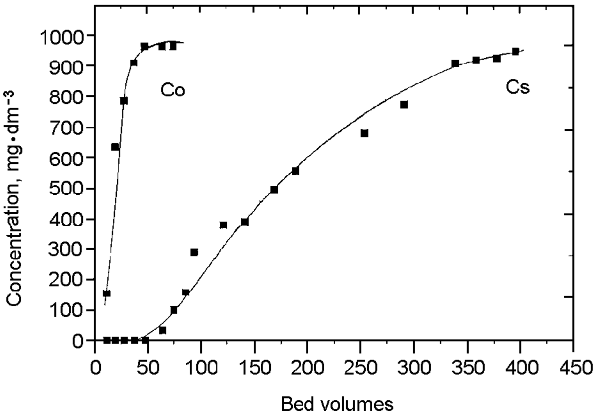


Fig. 7. Break-through curve of the simultaneous sorption of cesium and cobalt

Conclusions

It has been revealed that the KNiFC inorganic ion exchanger, which we have synthesized, has a high chemical and thermal stability in the pH range 1–5.5. The successful laboratory utilization of KNiFC beds for the fixed bed technique showed that they have an adequate mechanical strength. The KNiFC is more selective for cesium than for cobalt. Therefore, the selective separation of cesium from solutions contaminated with cobalt is feasible by KNiFC.

References

1. H. F. ALY, M. A. EL-ABSY, E. S. ZAKARIA, I. M. EL-NAGGAR, Proc. Intern. Conf. on Radioactive Waste Management and Environmental Remediation-ICEM, Vol. 1, ASME, New York, 1995, p. 371.
2. I. M. EL-NAGGAR, M. ABDEL-HAMID, S. A. SHADY, H. F. ALY, Proc. Intern. Conference on Radioactive Waste Management and Environmental Remediation-ICEM, Vol. 1, ASME, New York, 1995, p. 367.
3. J. C. MILLER, L. A. OLSON, K. C. JOHNSON, Sep. Sci. Technol., 32 (1997) No. 1–4, 37.
4. Y. V. KARLIN, L. B. PROZOROV, V. Y. CHUIKOV, V. N. KROPOTOV, Proc. of the 1995 MRS Fall Meeting, Boston, MA, 1996.
5. I. J. SINGH, B. M. MISRA, Sep. Sci. Technol., 31 (1996) No. 12, 1695.
6. S. VLASSELAR, W. D'OLIESLAGER, M. D'HAUT, J. Inorg. Nucl. Chem., 38 (1976) 327.
7. C. KONECNY, R. CALETKA, J. Radioanal. Chem.,14 (1973) 255.
8. K. WATARI, K. TANI, M. IZAWA, J. Nucl. Sci. Technol., 4 (1967) 190.
9. H. MIMURA, J. LEHTO, R. HARJULA, J. Nucl. Sci. Technol., 34 (1997) No. 6, 582.
10. H. MIMURA, J. LEHTO, R. HARJULA, J. Nucl. Sci. Technol., 34 (1997) No. 6, 607.
11. W. E. PROUT, E. R. RUSSELL, H. J. GROH, J. Inorg. Nucl. Chem., 27 (1965) 473.
12. S. KAWAMURA, H. KURTOTAKI, M. IZAWA, Bull.Chem. Soc. Japan, 42 (1969) 3003.
13. N. J. HESS, J. H. SUKAMOT, S. D RASSAT, R. T. HALLEN, R. J. ORTH, M. A. LILGA, W. E. LAWRENCE, Proc. of the 1996 MRS Fall Meeting, Boston, MA, 1997.
14. I. M. ISMAIL, M. R. EL-SOUROUGY, N. ABDEL-MONEIM, H. F. ALY, J. Radioanal. Nucl. Chem., to be published.
15. P. J. GELLINGS, Z. Phys. Chem. (Frankfurt), 54 (1967) 296.
16. International Center for Diffraction Data, Powder Diffraction File, Inorganic Phases, JCPDS, 1986.
17. M. R. SHAHBANDEH, The ion exchange properties of complex cyanoferrates, Ph.D Thesis, University of London, 1980 and references cited there.
18. J. B. AYERS, W. H. WAGGONER, J. Inorg. Nucl. Chem., 33 (1971) 721.