JOURNAL OF SOLID STATE CHEMISTRY **141,** 475–485 (1998)
ARTICLE NO. SC987997

Sorption Mechanisms of Cesium on $Cu^{II}_2Fe^{II}(CN)_6$ and $Cu^{II}_3[Fe^{III}(CN)_6]_2$ Hexacyanoferrates and Their Relation to the Crystalline Structure

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Received March 16, 1998; in revised form August 4, 1998; accepted August 12, 1998

$Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$ and $Cu^{II}_3[Fe^{III}(CN)_6]_2 \cdot xH_2O$ can be prepared with reproducible chemical compositions and structures after careful washing. They have cubic *Fm$\bar{3}$m* structures with iron vacancies. In $Cu^{II}_2Fe^{II}(CN)_6$, copper occupies two different sites: Cu1 in position 4*b* linked to Fe through the CN groups, and Cu2 not linked to the CN groups and partially occupying the interstitial 24*e* positions. The second type of site is not present in $Cu^{II}_3[Fe^{III}(CN)_6]_2$. Sorption kinetics and isotherms were determined for cesium on both hexacyanoferrates by batch experiments. On $Cu^{II}_3[Fe^{III}(CN)_6]_2$, the maximum uptake is only 0.073 Cs/Fe (at./at.). On $Cu^{II}_2Fe^{II}(CN)_6$, the uptake reaches 1.5 Cs/Fe. The sorption kinetics include at least two steps: a $t^{1/2}$ variation until approximately 72 h and then a slow evolution studied up to 6 months. The sorption mechanism is complex. The main process seems to be diffusion of ion pairs, followed by a reorganization of the solid, resulting in one or more new solid phases. The presence of the Cu2 site seems to play a favorable role in the sorption. Owing to its good midterm stability and the first rapid step of exchange, $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$ seems to be one of the most promising compounds for the recovery of cesium from nuclear liquid wastes. © 1998 Academic Press

INTRODUCTION

^{137}Cs ($T_{1/2} \sim 30$ y) and ^{135}Cs ($T_{1/2} \sim 2 \times 10^6$ y) are among the main fission products in radioactive wastes. Hexacyanoferrates(II) and -(III) of several transition metals have a high affinity for cesium over a wide pH range and good resistance to ionizing radiation (1–6). Although the preparation and use of hexacyanoferrates for the removal of cesium from solutions by sorption or precipitation have been studied over the past 40 years, the results remain mostly empirical and the choice of the best composition of the solid and the most efficient procedure is not yet obvious (7, 8). One of the reasons for this uncertainty is that hexacyanoferrates exhibit a great variety of compositions and structures. Several stoichiometries may be obtained with the same transition metal, depending on the method of preparation, and it is therefore difficult to establish any relationship with the sorption properties observed.

In an effort to clarify this situation, we previously performed a systematic study of the preparation methods, compositions, and structures of zinc and nickel hexacyanoferrates (II) (9,10) and, more recently, of copper hexacyanoferrates (II) and -(III) (11). The industrial applications of such products are inevitably connected to the isolation of compounds with reproducible properties. Before undertaking a systematic study of the sorption properties of copper hexacyanoferrates, we turned our attention first to synthesis methods, with the aim of defining reproducible preparative methods which give pure compounds (12).

The decomposition of hexacyanoferrates has been suspected to be responsible for the evolution of gases at Hanford (13). Clearly, the development of decontamination methods requires detailed understanding of the sorption processes, referred here to all processes by which a species dissolved in solution is transferred to a solid suspended in that solution. A study of the sorption mechanisms of cesium on zinc and nickel hexacyanoferrates(II) showed that the process strongly depends on the composition and crystal structure of the starting solid (14). The sorption may result from a true ion exchange or take place with a change of phase. These different mechanisms lead to different sorption kinetics, capacities, and stability of the solids, factors which have an important impact on the choice of the most suitable compounds and on experimental conditions for industrial applications. The Loviisa power plant (Finland) is the only site at which cobalt hexacyanoferrate columns have been used and no information is available on their long-term performance (6). Further studies are needed to describe the mechanisms of cesium fixation on hexacyanoferrates, why

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0022-4596/98 $25.00

some of the compounds are unstable, and their long-term evolution.

The copper hexacyanoferrate phases most often observed are cubic $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$ and $Cu^{II}_3[Fe^{III}(CN)_6]_2 \cdot xH_2O$. Monoclinic $Na_2Cu^{II}Fe^{II}(CN)_6 \cdot 10H_2O$ and triclinic $K_2Cu^{II}Fe^{II}(CN)_6$ are also known (12,15). The purpose of the present work is to study the sorption mechanisms of cesium on $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$ and $Cu^{II}_3[Fe^{III}(CN)_6]_2 \cdot xH_2O$, both of which can be prepared as pure phases by precipitation from aqueous solutions (12). We assess their efficiency toward cesium fixation, select the most suitable compound for long-term storage, and improve our understanding of the fixation mechanisms.

MATERIALS AND METHODS

Preparation of Copper Hexacyanoferrates

Two methods of preparation could be successfully used: precipitation and local growth (16–18). However, owing to the simplicity, good yields, and reproducibility noted for the preparation of $Cu^{II}_2Fe^{II}(CN)_6$ by precipitation (12), this route was the only one used for this compound in this study.

$Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$. This compound was prepared by precipitation according to a method derived from Kawamura *et al.* (19). A 0.125 M lithium or sodium hexacyanoferrate(II) solution and a 0.375 M copper(II) nitrate solution were poured simultaneously (atomic ratio Cu/Fe = 3) into deionized water at 50°C. The slurries obtained were washed with deionized water and separated by decantation. This process was repeated at least eight times. The precipitate was allowed to dry in air. Sieves (200, 100, and 25 μm) were then used and the various fractions dried in air at room temperature (12).

$Cu^{II}_3[Fe^{III}(CN)_6]_2 \cdot xH_2O$. This compound was prepared by precipitation (20) by mixing a 0.125 M potassium hexacyanoferrate(III) solution and a 0.375 M copper(II) nitrate solution with the atomic ratio Cu/Fe = 3. The slurries were washed and separated in a similar way.

Alternatively, preparation by local growth was used: potassium hexacyanoferrate(III) (200 g) was placed in a solution of copper(II) sulfate (1.4 M, 1 L) and maintained at 45°C for 2 days. The granular product was washed thoroughly with water. The majority of the particles have dimensions greater than 100 μm.

Chemical Analysis

Nondestructive neutron activation analyses (NAA) were systematically performed for the determination of Na, K, Cu, and Fe using the facilities of the Pierre Süe Laboratory. The water content was derived by difference, considering that one Fe atom is bound to six cyanide groups, and the results were confirmed by thermogravimetric analysis. For a complete determination of anions, some products were analyzed at the Service Central d'Analyses (CNRS, Vernaison, France).

The starting compounds were also analyzed for Na, K, Cu, and Fe by inductively coupled plasma atomic emission spectroscopy (ICP/AES). Samples (20 mg) were dissolved in 11.6 M $HClO_4$ prior to analysis.

Other Characterization Methods

Morphology. Optical microscopy and scanning electron microscopy (SEM) were used to characterize the morphology. Samples were deposited on aluminum plates and examined by a Stereoscan electron microscope (Cambridge Instruments).

Specific surface area measurements. Nitrogen adsorption–desorption isotherms were obtained at 77 K with a Sorptomatic Series 1800 apparatus (Carlo Erba Instruments). Samples were outgassed at 60°C at $< 10^{-4}$ mmHg overnight. The results were interpreted using the BET (Brunauer, Emmet, and Teller) method (21) and the Dubinin–Radushkevitch calculation, appropriate for microporous materials (22).

X-ray crystallographic analyses. Powder X-ray diffraction patterns were recorded using a Siemens D500 diffractometer and a Cu$K\alpha$ X-ray radiation. The identification of the phases was made by reference to the JCPDS-ICDD database (release 1995). The powder diffraction patterns were simulated and fitted using Cerius (release 1.5) software from Molecular Simulations Inc.

Infrared (IR) spectroscopy. Infrared spectra were recorded in the range 400–4000 cm^{-1} on samples diluted in KBr using a Bomem DA8 FTIR instrument. Preliminary experiments using transmission and reflectance methods with Nujol or KBr showed no difference between the resulting spectra in the region 2000–2200 cm^{-1}.

Cesium Sorption

Radioactive ^{134}Cs was obtained by irradiating cesium nitrate in the neutron flux of the Orphee reactor using the facilities of the Pierre Süe Laboratory at Saclay.

Fractions (25 mg) of the hexacyanoferrate studied were added to 5 mL of either deionized water or 0.1 M HNO_3 containing known concentrations of radioactively labeled cesium. Some experiments were also performed in 0.14 M $LiBO_2$ solutions at pH 8 to simulate the solutions used in pressurized water nuclear reactors (PWR). The fractions were shaken mechanically for a predetermined time. The solid was recovered on a 0.2-μm porosity filter (mixed ester cellulose ME24ST Schleicher and Schull filters) and the quantity of cesium sorbed was determined by measuring the radioactivity of an aliquot of the solution.

Identical experiments, but without radioactive tracer, were used to measure the composition of the filtrates and the recovered solids (washed with deionized water and air-dried at room temperature). The release of cations from the solid into the solution was monitored by analysis for Cu, Fe, and K by ICP/AES. The solids were analyzed by NAA for Cu, K, and Cs and by ICP/AES after dissolution for Cu, Fe, and K. Some recovered solids were submitted to X-ray diffraction patterns.

For kinetics experiments, the initial cesium concentration was constant in all solutions and equal to 2 mol of Cs per mol of Fe (0.02 M $CsNO_3$) in the hexacyanoferrate; the time of shaking ranged from a few minutes to 1 month.

To determine sorption isotherms, the initial mole ratio varied from 0 to 2 Cs per Fe (from 0 to 0.02 mol L^{-1}) for a shaking time of 1 month.

Complementary long-term kinetic measurements were performed on $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$ using twin experiments (one with inactive cesium and another one with labeled ^{134}Cs). One gram of solid was placed in 500 mL of the same solutions as above containing cesium nitrate (8×10^{-3} M $CsNO_3$; atomic ratio Cs : Fe = 2). Aliquots (1 mL) of the solution were taken at regular intervals and filtered, and the radioactive cesium or inactive copper and iron contents were determined in the solution. Measurements were performed for periods up to 7 months.

RESULTS

Characterization before Sorption

Morphology. For the products prepared by precipitation at the laboratory scale (quantity prepared < 100 g), the particles have dimensions ranging between 10 μm and 1 mm (with ~ 90% larger than 100 μm) with irregular shapes and surfaces. In the case of semi-industrial preparations (~ 20 kg), drying was performed at 80°C, which causes the particles to agglomerate, and the fraction of particles with dimensions larger than 1 mm is high. The size of the agglomerates prepared by local growth was between 100 and 200 μm. The mechanical strength of these aggregates when they are shaken in solution is low.

The magnification obtained using electron microscopy did not allow any observation of crystallites in the products (main dimension < 0.2 μm). For precipitated powders the crystallite size from X-ray diffraction and Cerius software is estimated to be between 100 and 200 Å.

Chemical composition. The chemical compositions of the products used for cesium sorption experiments are given in Table 1. Compositions close to $Cu^{II}_2Fe^{II}(CN)_6$ and $Cu^{II}_3[Fe^{II}(CN)_6]_2$ were obtained. For example, starting from $Li_4Fe^{II}(CN)_6$, $Cu^{II}_2Fe^{II}(CN)_6$ is always obtained with a yield approaching 100%; using $K_3Fe^{III}(CN)_6$, a composition close to $Cu^{II}_3[Fe^{III}(CN)_6]_2$ was reached (12). Some alkaline elements present as impurities in alkaline hexacyanoferrates were sometimes found at low concentration in the solid.

TABLE 1
Preparation Methods and Chemical Compositions of Copper Hexacyanoferrate Powders Used for Cesium Sorption

Sample code	Alkaline hexacyano-ferrate used	Preparation method	Chemical composition
Cu93.10	$Li_4Fe(CN)_6$	Precipitation	$K_{0.03}Na_{0.01}Cu_{1.83}Fe(CN)_6 \cdot 8.5H_2O^a$
Cu93.14	$Na_4Fe(CN)_6$	Precipitation	$K_{0.01}Na_{0.03}Cu_{1.94}Fe(CN)_6 \cdot 15.7H_2O^a$
Cu94.1	$Li_4Fe(CN)_6$	Precipitation	$Na_{0.03}Cu_{2.01}Fe(CN)_6 \cdot 9.5H_2O^a$
Cu95.1	$Li_4Fe(CN)_6$	Precipitation	$Cu_{2.01}Fe(CN)_6 \cdot 13.9H_2O^a$
Cu95.7	$Li_4Fe(CN)_6$	Precipitation	$Cu_{1.98}Fe(CN)_6 \cdot 8.7H_2O^a$
Cu89.13	$K_3Fe(CN)_6$	Local growth	$K_{0.07}Cu_{1.51}Fe(CN)_6 \cdot 4.9H_2O^b$
Cu93.29	$K_3Fe(CN)_6$	Precipitation	$K_{0.04}Cu_{1.39}Fe(CN)_6 \cdot 5.3H_2O^b$

[a] Closest stoichiometric formula $Cu_2Fe^{II}(CN)_6$.
[b] Closest stoichiometric formula $Cu_3[Fe^{III}(CN)_6]_2$.

$Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$

The compounds recovered were generally washed with deionized water (pH ~5–6). In the case of the preparation denoted Cu93.10 in Table 1, the composition is deficient in copper, and the charge is apparently not compensated by the presence of another metal cation (absence of sodium and potassium). The replacement of copper ions by protons could be suspected, owing to the large volume of deionized water used in washing (23). This phenomenon was not observed when the product was washed with deionized water, the pH of which was previously adjusted to 8 with LiOH (products Cu95.1 and Cu95.7).

The water content of $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$ is high, with x varying between 8 and 16 H_2O molecules per iron atom.

Several authors have reported a final composition that includes variable quantities of sodium in copper hexacyanoferrates(II) (11) when starting from a $Na_4Fe(CN)_6$ solution. This was investigated here by preparing a compound using solutions of $Na_4Fe(CN)_6$ and copper nitrate with a mole ratio Cu : Fe = 3. In this case, the product yield calculated on the mass of product with particle sizes > 25 μm is only approximately 50%. For the mole ratio Cu : Fe = 1, the yield is even lower. The compositions of the powder before and after washing and of the wash solutions were analyzed (Table 2). Before washing, the sodium content is high and the existence of a mixture of phases (sodium copper hexacyanoferrates, copper hexacyanoferrates, or other sodium salts) in the solid could be suspected from this global composition. After careful washing, the content of sodium fell drastically. Since copper hexacyanoferrates are

TABLE 2
Influence of the Washing Volume on the Atomic Composition of the Solids[a]

Initial mole ratio in solution	Washing volume (L)	Na : Fe (at. : at.)	Cu : Fe (at. : at.)	Product
Cu : Fe = 1 Na : Fe = 4	< 0.1	1.01	1.93	Cu90.15
Cu : Fe = 3 Na : Fe = 4	< 0.1	0.21	2.06	Cu93.27
Cu : Fe = 3 Na : Fe = 4	4	0.01	2.13	Cu93.27

[a] Nitrate content not determined.

very insoluble, no soluble $Fe(CN)_6^{4-}$ complexes could be suspected.

The composition of the solid after washing is close to $Cu_2Fe(CN)_6$. In the washing solutions, the presence of iron, sodium, and copper could be detected with a Na : Cu ratio = 1.95 and explained by the formation of fine particles of sodium copper hexacyanoferrate which are removed by washing. The higher the alkali metal to copper ratio, the higher the proportion of this small particulate hexacyanoferrate(II) and the lower the overall yield. Finally, after careful washing (Table 2), sodium is eliminated. However, the Cu : Fe ratio is higher than 2 and indicates the presence of anions such as nitrates remaining from the starting components. The possibility of inserting anions will be discussed later.

$Cu_3^{II}[Fe^{III}(CN)_6]_2 \cdot xH_2O$

The compositions are given in Table 1. The precipitated product Cu93.29 was used for sorption experiments. The local growth method gave similar compositions (12), with a ratio Cu : Fe close to 1.5.

The water content of $Cu_3^{II}[Fe^{III}(CN)_6]_2 \cdot xH_2O$ is lower than that of $Cu_2^{II}Fe^{II}(CN)_6 \cdot xH_2O$, generally about 5 H_2O molecules per Fe atom.

Structure. The powder diffraction patterns of Cu93.14 and Cu89.13 coincide with JCPDS-ICDD 1.0244 and 23.0214, respectively, but with some discrepancies (Fig. 1). Both types of spectra can be attributed to the cubic structure. However, they show a certain number of additional weak lines that could not be indexed within the interpretation of a cubic structure. All attempts to refine these two compounds in a less symmetrical system (rhombohedral or tetragonal) led to misleading results. Two hypotheses can be formulated: either the products contain a small quantity of impurities or the stoichiometric formulae cover two

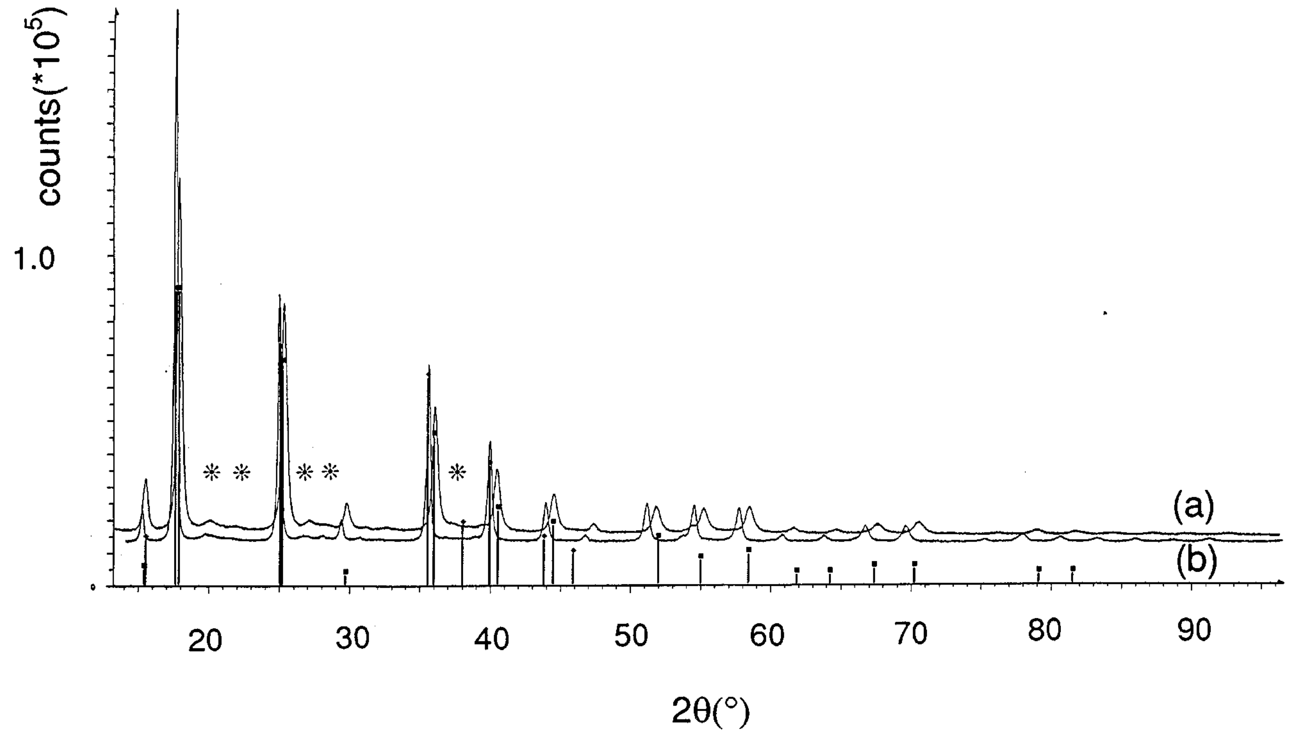

FIG. 1. XRPD patterns for (a) $Cu_2^{II}Fe^{II}(CN)_6 \cdot xH_2O$ (Cu95.1) and (b) $Cu_3^{II}[Fe^{III}(CN)_6]_2 \cdot xH_2O$ (Cu89.13) with additional weak lines (*) and comparison with JCPDS-ICDD 1.0244 (■) and 23.0214 (◆).

different phases that can exist simultaneously. The latter situation was also encountered for $Zn_2Fe^{II}(CN)_6$ and $Zn_3[Fe^{III}(CN)_6]_2$, which present two different structures, cubic and rhombohedral (24).

$Cu_2^{II}Fe^{II}(CN)_6 \cdot xH_2O$

Single crystals of this compound could not be prepared by diffusion in a silicate gel unlike in the case of $M^I_2CuFe^{II}(CN)_6$ (M^I = Na,K) (23). The structure was therefore determined using the powder diffraction patterns. $Cu_2^{II}Fe^{II}(CN)_6 \cdot xH_2O$ is cubic, space group $Fm\bar{3}m$, having a disordered structure with vacancies among iron sites (Table 3 and Fig. 2). Vacancies can be occupied by water or salt molecules. Copper atoms occupy two types of site (15). Copper atoms Cu1 forming square-planar CuN_4 complexes are linked through cyanide bridges to FeC_6 octahedra, leading to the frequently reported lattice parameter of ~ 10 Å. The Cu2 atoms, with fractional coordinates 1/4, 1/4, 1/4, are not linked to iron by cyanide bridges and are expected to be more mobile than the Cu1. This second type of site presents vacancies.

A background is observed under the diffractogram (Fig. 1). It may be due either to the presence of impurities or to other amorphous or poorly crystalline hexacyanoferrate phases. This background is reduced after 12 h of contact with a 0.1 M HNO_3 solution. A small amount of Cu (approximately 0.05 mol per mol) was detected in 0.1 N HNO_3 solutions, equilibrium being reached after only a few hours of contact. However, the composition of the solid after drying does not indicate any change within the analytical errors. In contrast, in water or $LiBO_2$ solutions, no dissolved copper was detected even after several months.

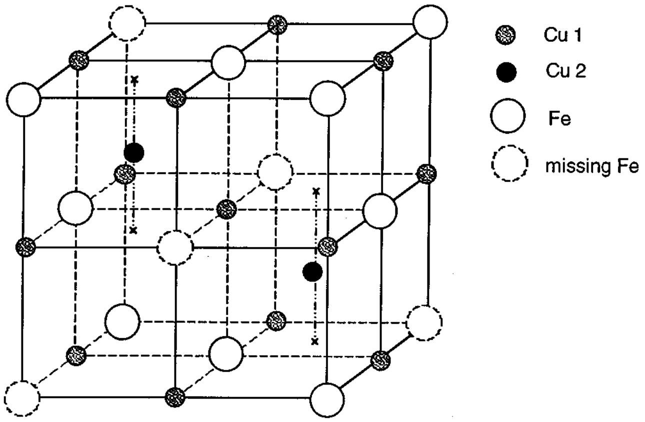

FIG. 2. Structure of cubic $Cu_2^{II}Fe^{II}(CN)_6 \cdot xH_2O$, space group $Fm\bar{3}m$ ($a \sim 10.0$ Å; $z = 2 + 2/3$).

TABLE 3

Fractional Atomic Coordinates and Site Occupancy Parameters for $Cu_2^{II}Fe^{II}(CN)_6 \cdot xH_2O$ and $Cu_3^{II}[Fe^{III}(CN)_6]_2 \cdot xH_2O$ (Water Molecules Are Not Included)

	Fractional atomic coordinates			
Atom	x/a	y/b	z/c	Site occupancy
		$Cu_3^{II}[Fe^{III}(CN)_6]_2 \cdot xH_2O^a$		
Fe 4*a*	0	0	0	2/3
Cu 4*b*	1/2	0	0	1
C 24*e*	0.212(3)	0	0	2/3
N 24*e*	0.3200(7)	0	0	2/3
		$Cu_2^{II}Fe^{II}(CN)_6 \cdot xH_2O^b$		
Fe 4*a*	0	0	0	2/3
Cu1 4*b*	1/2	0	0	1
Cu2 8*c*	1/4	1/4	1/4	1/6
C 24*e*	0.197(4)	0	0	2/3
N 24*e*	0.311(3)	0	0	2/3

[a] $Fm\bar{3}m$; $a = 10.1049(2)$ Å; $z = 1 + 1/3$.
[b] $Fm\bar{3}m$; $a = 9.9860(3)$ Å; $z = 2 + 2/3$.

$Cu_3^{II}[Fe^{III}(CN)_6]_2 \cdot xH_2O$

Very small cubic single crystals (average dimensions: 1–2 μm) of $Cu_3^{II}[Fe^{III}(CN)_6]_2 \cdot xH_2O$ were obtained in a gel containing sodium silicate and potassium hexacyanoferrate(III) in contact with a cupric nitrate solution (12).

All powdered samples obtained gave similar X-ray diffraction patterns. $Cu_3^{II}[Fe^{III}(CN)_6]_2 \cdot xH_2O$ is cubic $Fm\bar{3}m$ (20,25) with $z = 1 + 1/3$, leading to a disordered structure, with vacancies in Fe sites (Table 3). The structure resembles that of $Cu_2^{II}Fe^{II}(CN)_6 \cdot xH_2O$ but, here, only Cu1 sites are occupied, suggesting less exchange possibilities.

Specific surface area. The specific surface area was measured on the preparations coded Cu94.1 and Cu89.13. In both cases, the shape of the nitrogen adsorption–desorption isotherm is characteristic of a microporous solid, with a little contribution of mesopores (Types I and IV in the IUPAC classification). The BET specific surface area of Cu94.1 was $972\,m^2\,g^{-1}$ (Langmuir surface area $1010\,m^2\,g^{-1}$) with a micropore volume of $0.391\,cm^3\,g^{-1}$. The BET specific surface area of Cu89.13 was calculated to be $643\,m^2\,g^{-1}$. The pore volume corresponds quite closely to that which can be calculated from thermogravimetry as corresponding to the volume occupied by water molecules and strongly suggests that the microporosity becomes accessible on removing water from the zeolitic-like cavities. If the BET values are normalized to the molecular weight, the surface area is close to $4.9 \times 10^5\,m^2$ per Fe atom for Cu94.1 and $2.0 \times 10^5\,m^2$ per Fe atom for Cu89.13. These values are particularly high, the greater values being observed for $Cu_2^{II}Fe^{II}(CN)_6$. It is interesting to note that the ratio of BET surface areas is 2.5, close to the ratio of the number of water molecules per Fe atom.

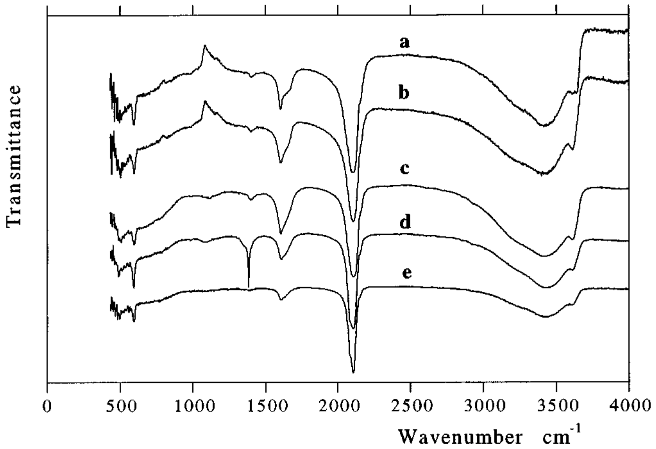

FIG. 3. Infrared spectra of copper hexacyanoferrates before and after cesium sorption: (a) $Cu^{II}_3[Fe^{III}(CN)_6]_2 \cdot xH_2O$ (Cu89.13); (b) $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$ (Cu95.1); (c) $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$ (Cu95.1) after 7 months of contact with a solution of 0.1 M HNO_3; (d) $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$ (Cu95.1) after 7 months of contact with a solution of 0.1 M $CsNO_3$ in 0.1 M HNO_3; (e) same product after washing with water.

Infrared spectroscopy. In the IR spectrum of $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$, the stretching vibration $\nu(C{\equiv}N)$ is observed at 2106 cm^{-1} (Fig. 3b), close to its position in, e.g., $K_4Fe^{II}(CN)_6$. A weak and ill-defined shoulder is observed at 2160 cm^{-1}. A broad band of maximum at 3422 cm^{-1} arises from the O–H stretching vibrations of water molecules and is accompanied by the deformation mode $\delta(H_2O)$ at 1605 cm^{-1}. Following suspension in HNO_3 (0.1 M) for 7 months (Fig. 3c), the position of the cyano stretch is unchanged, inferring no change in the oxidation state of Fe^{II}. No evidence is seen of the formation of H_3O^+, which might have been expected from the apparent loss of Cu(II) indicated above. The spectrum of copper hexacyanoferrate(III) (Fig. 3a) in the region 2100–2500 cm^{-1} is very similar to that of hexacyanoferrate(II). The absorption bands in the region 2080–2200 cm^{-1} are all due to the stretching vibration of the CN bond. The absorption maximum is at ca. 2100 cm^{-1} for both $Fe^{III}(CN)_6$ and $Fe^{II}(CN)_6$ although, in addition, a more intense shoulder at 2166 cm^{-1} is observed for the former (Fig. 3b).

All the IR spectra of the starting products present a weak vibration band between 1385 and 1400 cm^{-1}, probably connected to the presence of nitrates used in syntheses.

Sorption on $Cu^{II}_3[Fe^{III}(CN)_6]_2 \cdot xH_2O$

Fixation of 0.06–0.08 Cs/Fe is reached after 10 min and remains constant even after a contact time of several hours (Table 4). The mechanism of cesium fixation on this compound could be a sorption limited to the superficial layers of the solid owing to the fast kinetics and the low quantities sorbed. This result does not correspond to those published by other authors (Table 5). This discrepancy is explained by the method used by Ganzerli *et al.* (26) for determining the sorption capacity (coprecipitation instead of sorption); Jain *et al.* (27) studied a mixed copper potassium hexacyanoferrate(III) different from the simple copper hexacyanoferrate(III) used here.

TABLE 4
Sorption of Cesium on $Cu^{II}_3[Fe^{III}(CN)_6]_2$ (Cu93.29) in 0.1 M HNO_3[a]

Shaking time (min)	Cs : Fe in the solid (at. : at.)[b]
5	0.028 ± 0.008
10	0.060 ± 0.002
300	0.073 ± 0.007

[a] Initial ratio of cesium in solution to iron in the solid = 1.5.
[b] Mean value of two measurements.

Sorption on $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$

Maximum uptake. The maximum uptake is indicated in Table 5, together with some literature values. Our values are higher than those published, but this can be easily explained by radically different times of contact. Somewhat different values can be obtained when starting from different preparations of the same compound.

Kinetics. The sorption kinetics of cesium on $Cu_2Fe(CN)_6$ in 0.1 M HNO_3 is shown in Fig. 4 as a function of time, including the measurements up to 1 month and the complementary measurements up to 6 months. A $t^{1/2}$ time scale was chosen to expand the smallest time intervals. The quantities retained are always higher than those observed

TABLE 5
Maximum Uptake of Cesium[a] on Various Copper Hexacyanoferrates(II) and- (III)

Sorbent	5 < pH < 8	HNO_3 0.1 N	Contact time	Ref.
$Cu^{II}_2Fe^{II}(CN)_6$	0.99[b,c]	1.50[d]	6 months	our results
	1.05[c]	1.34[c]	6 months	our results
$Cu^{II}_2Fe^{II}(CN)_6 \cdot 2.5H_2O$	0.78		1 h	(28)
$Cu^{II}_2Fe^{II}(CN)_6$	0.5		precipitation *in situ*	(29)
$Cu^{II}_2Fe^{II}(CN)_6 \cdot 12H_2O$[e]	0.5		4 h	(26)
$Cu^{II}_3[Fe^{III}(CN)_6]_2$		0.073[f]	5 h	our results
$Cu^{II}_3[Fe^{II}(CN)_6]_2 \cdot 14H_2O$	1[g]		4 h	(26)
$KCu^{II}Fe^{III}(CN)_6 \cdot 5H_2O$	0.89		48 h	(27)

[a] In Cs atoms per Fe atom.
[b] $LiBO_2$ solution.
[c] Cu94.1.
[d] Cu95.1.
[e] Na = 2% weight.
[f] Cu93.29.
[g] Mixed cesium–copper hexacyanoferrate(III) prepared by precipitation.

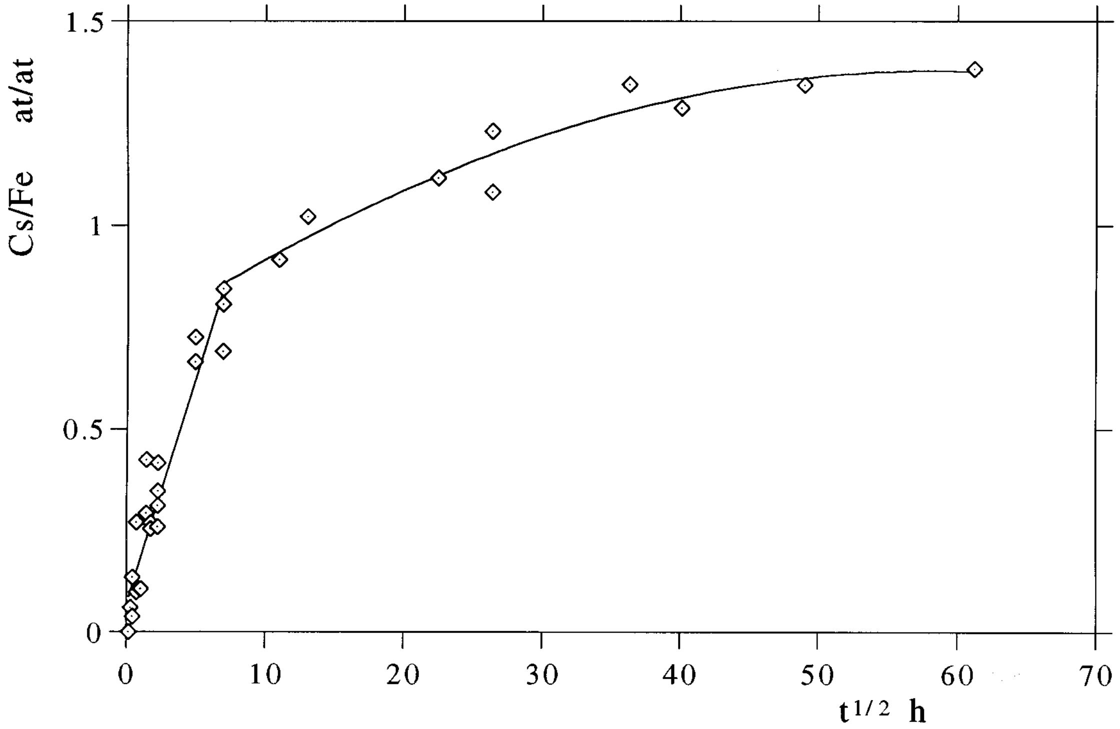

FIG. 4. Sorption kinetics of Cs on $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$ (Cu93.10, Cu93.14, and Cu94.1) in 0.1 M HNO_3 solution expressed as the variation of the sorbed quantity of Cs atoms per atom of iron as a function of the square root of time. Initial mole ratio Cs in the solution: Fe in the solid = 2; maximum shaking time: 6 months.

with copper hexacyanoferrates(III), except in the first minutes of the experiments, when they are similar. At least two steps may be observed in the kinetics. In the first one, which lasts approximately 3 days, the sorbed concentration is proportional to the square root of contact time; an uptake of 0.8 Cs : Fe is achieved at this step (~ 1.6 meq $\cdot$ g^{-1}). A $t^{1/2}$ variation is often interpreted by a diffusional process. In the second step, a slower evolution of the solid is observed. No steady state of the sorbed quantity is noted even after 6 months. The sorbed concentration varied as a function of time with the same steps and variation in water containing or not $LiBO_2$, but with lower sorbed quantities. The uptakes at 6 months are indicated in Table 6.

Sorption kinetic experiments were performed either directly with the solid or with the solid previously treated by stirring 17 h in aqueous HNO_3 or $LiBO_2$ solutions before addition of cesium nitrate. The uptake is faster with a product preconditioned in HNO_3 during the first minutes of experiments, but there is no difference after a few hours. This phenomenon is not observed in the neutral solution of $LiBO_2$.

Sorption balance. Since no steady state of sorption was achieved even after 6 months, the variation of the sorbed quantity as a function of the initial concentration of cesium in the solution at 1 month of contact does not represent a true sorption isotherm. The results shown in Fig. 5 were obtained in 0.1 M HNO_3 solution and for a deionized water solution. To understand the stoichiometry of the process, we have indicated the variations of the sorbed cesium (Cs_S), of copper in the solid (Cu_S), and of copper in the liquid (Cu_l) as well as the sum of cations in the solid [$(Cs + Cu)_S$]. All concentrations are referred to one Fe atom in the solid. The straight line of slope 1 drawn in Fig. 5 would correspond either to a 100% sorption yield or to a 1 : 1 Cs–Cu equivalent exchange.

We observe that, for both types of solution, the yield of sorption is close to 100% until the Cs : Fe ratio reaches 1 in the solid. The sum of cations (Cs + Cu) in the solid increases

TABLE 6
Mole Ratios (per Iron) in the Solids after a Contact Time of 6 months[a]

Medium	Cs	Cu	K	Li	B	NO_3^-
HNO_3	1.34 ± 0.10	1.37	0.007	nd[b]	nd[b]	0.029
$LiBO_2$	0.99 ± 0.07	1.99	0.003	0.028	0.630	0.035
H_2O	1.05 ± 0.08	1.54	0.001	nd[b]	nd[b]	0.019

[a] Starting sorbent: Cu94.1, phase $Cu^{II}_2Fe^{II}(CN)_6$.
[b] nd = not determined.

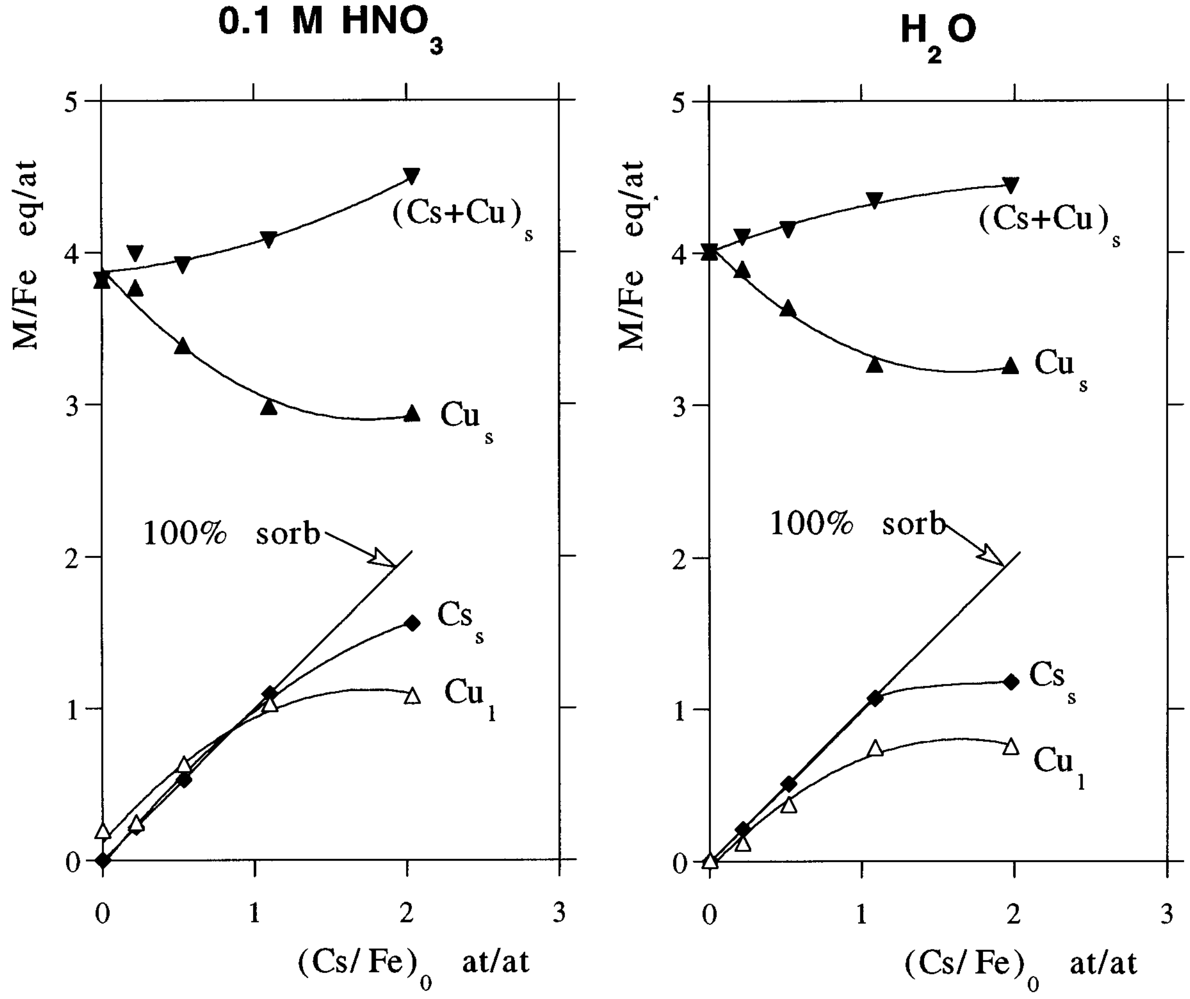

FIG. 5. Stoichiometry of the sorption of cesium on $Cu_2^{II}Fe^{II}(CN)_6 \cdot xH_2O$ (Cu95.1) in 0.1 M HNO_3 solutions and in deionized water after 1 month of contact. The variations of the sorbed cesium quantity (Cs_S), of copper in the solid (Cu_S), and of copper in the liquid (Cu_l) and the sum of cations in the solid [$(Cs + Cu)_S$] are represented as a function of the initial cesium concentration in the solution, $(Cs/Fe)_0$. All concentrations are referred to one Fe atom in the solid and expressed as equivalents per atom. The straight line of slope 1 would correspond either to a 100% sorption yield or to 1 : 1 Cs–Cu equivalent exchange.

as a function of the sorbed Cs content and exceeds the stoichiometry of 4 equiv per mol, expected to compensate the charge of $Fe(CN)_6^{4-}$. Some differences appear when comparing 0.1 M HNO_3 solution with water. More cesium is sorbed and more copper is released in acidic medium; in this case, a small quantity of copper is released without addition of cesium and the release of copper compensates the sorption of cesium until Cs : Fe = 1. For higher uptakes, no more copper is released, while the sorbed cesium is still increasing. In water, the quantity of released copper is always less than the quantity of sorbed cesium. No iron is found in either solution.

We have also measured the quantity of copper released into the solution for the first part of the kinetic experiments ($t < 5$ h) for HNO_3 and $LiBO_2$ solutions (Fig. 6). The straight line would correspond to 1 : 1 Cs–Cu equivalent exchange. Here, there is much less released copper than sorbed cesium, except for the very first points. In the case of $LiBO_2$ solutions, the copper concentrations are very small, since precipitation of copper borate occurs. In HNO_3 solutions, copper concentrations are higher but are far from compensating the sorption of cesium. We have already indicated that after a month of contact (Fig. 5), the release of copper compensates the sorption of cesium until Cs : Fe = 1. This means that sorption is a dynamic process in which the release of copper follows sorption after some delay. An interpretation of this phenomenon will be discussed later.

X-ray diffraction measurements. Measurements were performed on solids after cesium sorption (Fig. 7). In water,

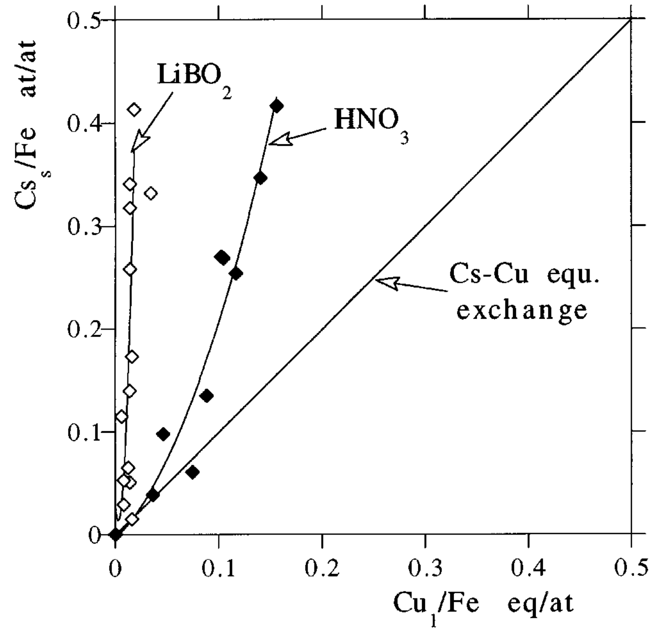

FIG. 6. Stoichiometry of the sorption of cesium on $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$ (Cu93.10) in 0.1 M HNO_3 solutions and in 0.14 M $LiBO_2$ solutions at pH 8 for kinetic experiments between 5 and 300 min of contact. The variations of the sorbed cesium quantity (Cs_S) are represented as a function of the concentration of copper released into the solution (Cu_l). All concentrations are referred to one Fe atom in the solid and expressed as equivalents per atom. The straight line of slope 1 would correspond to a 1:1 Cs–Cu equivalent exchange.

$LiBO_2$, or HNO_3 solutions, the fixation of cesium on $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$ leads to the destruction of the initial crystalline structure and the formation of one or more new phases. In the same media, but without cesium in solution, the X-ray diffraction pattern of $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$ is only slightly modified (see section Structure). One of these new phases contains diffraction lines similar in position to those observed by Kuznetsov *et al.* (30) for a cesium copper hexacyanoferrate(II) obtained by precipitation and with a proposed formula $Cs_2Cu_3[Fe(CN)_6]_2$ and a cubic structure. Following the precipitation method, a cesium copper hexacyanoferrate was prepared according to these authors (30). We observed a similar X-ray diffraction pattern to that reported, but the chemical analysis indicated a composition close to $Cs_2CuFe^{II}(CN)_6$ with large quantities of sodium and chlorine (atomic ratio Na : Fe = 0.5 and Cl : Fe = 0.2). In addition to the lines corresponding to those of "$Cs_2CuFe(CN)_6$," two other sets of lines (one set of two narrow lines; one set of broader lines) can be distinguished in the X-ray diffraction pattern of the solid recovered after Cs sorption onto $Cu_2Fe(CN)_6 \cdot xH_2O$. It is concluded that sorption of cesium leads to at least three new phases after 6 months of contact, only one of which is tentatively identified at present.

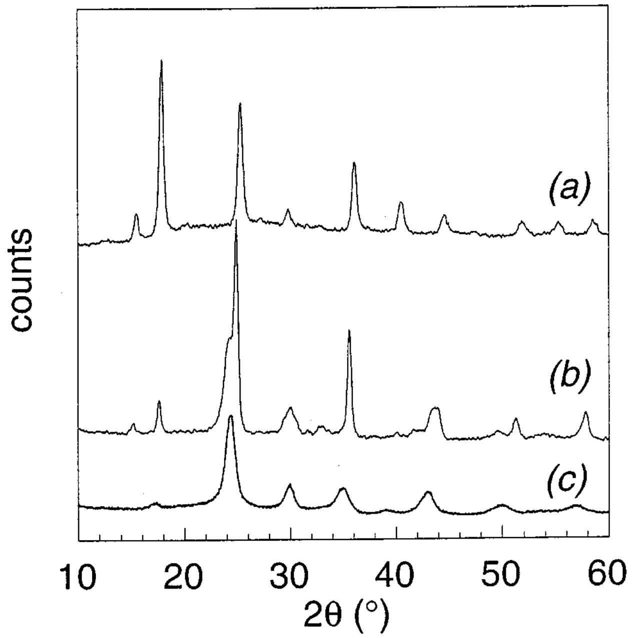

FIG. 7. X-ray diffraction patterns of (a) $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$ (Cu95.1), (b) same product after 7 months of contact with a solution of 0.1 M $CsNO_3$ in 0.1 M HNO_3, and (c) precipitated cesium copper hexacyanoferrate(II).

IR spectrometry. IR spectra of the solids were recorded after 6 months of contact with cesium in 0.1 M HNO_3 (Fig. 3d). No significant variation in the position on the band resulting from the CN vibration at 2100 cm^{-1} was observed, although a shoulder is noted at 2084 cm^{-1}. A sharp band of maximum at 1385 cm^{-1} indicates the presence of nitrate and suggests that Cs is, at least in part, sorbed in association with its counteranion. The intensity of this band is greatly reduced after further washing the Cs-sorbed sample with water (Fig. 3e). A decrease of the stretching and vibration bands of water in the 3600- and 1600-cm^{-1} regions, respectively, also results from the sorption of cesium.

DISCUSSION

The most striking feature is the difference between $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$ and $Cu^{II}_3[Fe^{III}(CN)_6]_2 \cdot xH_2O$, this last compound sorbing only a small amount of cesium. Both solids have similar structures, except that Cu2 sites are missing in the hexacyanoferrate(III). Therefore, these sites seem to play a favorable role in cesium sorption. This point shall be discussed later.

The most characteristic results for copper hexacyanoferrate(II) are a diffusion-type kinetics followed by a slow evolution which is still proceeding even after 7 months, cesium sorption not completely counterbalanced by release of copper with a time delay in this release, a (Cs + Cu) content in the solid which exceeds the stoichiometry allowed for hexacyanoferrates(II), the destruction of the initial structure with the formation of one or more new solid phases, and the presence of NO_3^- in the solid.

Since especially in the first step of the kinetics, the release of copper far from compensates the sorption of cesium, this element must be incorporated into the solid by a process which is neither ion exchange nor dissolution–precipitation. The most probable process, at least during the first hours of contact, is the incorporation of ion pairs: Cs^+ and NO_3^-. This explains the $t^{1/2}$ variation and the presence of NO_3^- in the solid. This incorporation is probably promoted by the high porosity of this compound, which has a BET surface area close to $1000\ m^2\ g^{-1}$ and presents Cu2 sites. The ion pairs are probably hosted in the vacancies of the structure, replacing the water molecules. We have effectively observed by chemical analyses and IR spectrometry a decrease of the water content as cesium sorption proceeds (molecular ratio $H_2O:Fe < 6$ after Cs sorption). Sorption of ion pairs was already mentioned by other authors (31–34) who explain this phenomenon by occupancy of vacant sites. The question arises why practically no sorption occurs with $Cu_3^{II}[Fe^{III}(CN)_6]_2$, which has a similar structure, but where all Cu2 sites are vacant. It is possible that metal ions are necessary to stabilize ion pairs in the porous structure of the solid. The BET surface area and the water content are lower in the $Cu_3^{II}[Fe^{III}(CN)_6]_2$ compound, with, however, the difference that sorption of cesium is excluded while water and nitrogen molecules can be incorporated.

At longer times or above a certain critical concentration of $CsNO_3$ in the solid, another process takes place leading to new solid phases accompained by the release of copper into the solution and by the destruction of the initial phase. At this step, sorbed NO_3^- ions can be released into the solution by washing, while cesium remains in the solid (Fig. 3d). This process proceeds slowly and we have not achieved its end point. The imbibition of salts from aqueous solutions into the interior of porous molecular sieve crystals (zeolites) is a well-known phenomenon (35). In the case of zeolites, it is easy to represent the inclusion as a Donnan membrane process (35). In our case, the quantity of sorbed anions remains small if compared to the quantity of sorbed Cs^+ and a new Cs-rich phase emerges rapidly. Salt sorption is a transitory phenomenon whose duration is short if compared to the long time required for the change of phase.

To estimate what would be the ultimate uptake of cesium, we have tried to prepare single crystals by slow diffusion of cesium hexacyanoferrate(II) in a lithium metasilicate gel containing copper tartrate crystals. Crystals were obtained, although too small for any structural study. Their composition, determined by energy-dispersive X-ray analysis on the SEM facility, was $Cs_{2.30}Cu_{0.92}Fe^{II}(CN)_6$. This is close to $Cs_2CuFe^{II}(CN)_6$, a phase that could be expected by analogy with the other alkaline copper hexacyanoferrates $Na_2CuFe^{II}(CN)_6 \cdot 10H_2O$ and $K_2CuFe^{II}(CN)_6$. Precipitation also leads to a composition close to $Cs_2CuFe^{II}(CN)_6$. However, this composition was never reached in our sorption experiments, indicating that the process slows down considerably after a ratio Cs/Fe of approximately 1.5 has been achieved, possibly because of limited speed of diffusion in the new phases. In fact, there is certainly a long time interval where both processes proceed together, ion pairs continuing to diffuse into the solid, while new phases are forming.

In HNO_3 solutions, we have observed a peculiar behavior leading to a small release of copper without addition of cesium and a higher cesium sorption than in deionied water for equivalent time intervals. One explanation may be a partial substitution of Cu2 sites by protons. These protons may then be exchanged by cesium ions. Such a process was observed in $Na_2Zn_3[Fe(CN)_6]_2$ (14). Here, it seems to play a minor role, but the overall sorbed quantity is higher than in neutral solutions. Another explanation may be a partial decomposition of the solid, promoting the fixation of cesium and the release of copper.

It remains to discuss the application of the above results to the removal of radioactive cesium from liquid wastes. We have measured the distribution coefficient of cesium on $Cu_2Fe^{II}(CN)_6$ after 24 h of contact in real effluents of the Osiris reactor at Saclay: it is superior to 20,000 in neutral solution. This high value shows that this product is suitable for the decontamination of nuclear wastes. However, we have measured a slight release of ions in the solutions where insoluble hexacyanoferrates have been stocked for several months. Possible structural changes of the products in aqueous solutions may be hazardous for very long term storage. The use of limited quantities of sorbent as well as complementary packaging strategies may be required. A possible solution could be the use of copper hexacyanoferrate(II) deposited on a mineral substrate such as silica with further vitrification treatment, for example (36–38).

CONCLUSION

$Cu_2^{II}Fe^{II}(CN)_6 \cdot xH_2O$ and $Cu_3^{II}[Fe^{III}(CN)_6]_2 \cdot xH_2O$ are easily prepared in powdered form both by precipitation and by local growth. Pure phases can only be obtained after a careful washing step. Erroneous interpretation of the composition can result from incomplete washing. They both have structures characterized by iron vacancies in the cubic $Fm\bar{3}m$ lattice. These two compounds differ from each other by the position of copper. In $Cu_2^{II}Fe^{II}(CN)_6 \cdot xH_2O$, two different sites exist; atoms Cu1 are linked to the CN network whereas atoms Cu2 are not. The second type of site is not present in $Cu_3^{II}[Fe^{III}(CN)_6]_2 \cdot xH_2O$.

$Cu_2^{II}Fe^{II}(CN)_6 \cdot xH_2O$ is stable, its structure remaining essentially unmodified even after several months in various solutions. It presents also the highest observed Cs uptakes.

The kinetics of cesium sorption show two steps. In the first ($t < 72$ h), cesium is rapidly sorbed with no equivalent release of copper. After several months of contact with cesium solutions, the emergence of a new phase can be detected from X-ray diffraction. The sorption mechanism is complex. It includes at least two steps: diffusion of ion pairs into the solid and formation of new solid phases. True ion exchange seems not to occur or plays a very minor role. Further complementary techniques such as Mössbauer spectrometry or extended X-ray absorption fine structure (EXAFS) will be used to increase our knowledge of these mechanisms.

$Cu^{II}_3[Fe^{III}(CN)_6]_2 \cdot xH_2O$ sorbs only small amounts of cesium. Although it has a structure similar to that of $Cu^{II}_2Fe^{II}(CN)_6 \cdot xH_2O$, the absence of Cu2 sites seems to prevent the diffusion of ion pairs into its structure.

Owing to the small quantities of cesium atoms present in radioactive effluents, all insoluble hexacyanoferrates are efficient sorbents. However, $Cu_2Fe(CN)_6 \cdot xH_2O$ seems to be one of the more promising compounds. It is easy to prepare by precipitation. The composition and the performances of the product are reproducible. The midterm stability in various solutions is good; the first rapid step of exchange and the rather high capacity of sorption allow its use for the decontamination of radioactive liquid wastes.

ACKNOWLEDGMENTS

S. A. thanks the Association pour la Recherche Scientifique (Ministère de l'Enseignement Supérieur et de la Recherche) and the STMI (Société des Techniques en Milieux Ionisants), France, for financial support. B.J. thanks the Human Capital and Mobility program for funding.

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