

Column-usable inorganic fixator preparation by localized growth on a solid alkaline ferrocyanide

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Inorganic fixators are selective sorbents which would often be preferred to commercial ion exchangers if they were suitable for column utilization. We present a new preparation method whose principle is a slow growth of an insoluble compound on a soluble-reacting crystal placed in a concentrated solution of another reactant. By this process, it is possible to prepare mixed zinc or nickel ferrocyanides by local growth on sodium or potassium ferrocyanide crystals placed in a concentrated zinc or nickel solution. The particle size is controlled by the size of the starting solid, the solution concentration and temperature. The growth mechanism seems to be a diffusion of water and divalent ions through the film of insoluble product formed around the soluble crystals. The reaction rate is increased by dilution of the solution or increase of its temperature. This method allows the preparation at low cost of insoluble ferrocyanide columns.

1. Introduction

Ferrocyanides are highly selective sorbents for heavy alkali metal ions, and can therefore be used to separate ^{137}Cs from other fission products [1, 2]. We have studied the retention phenomena on some nickel and zinc ferrocyanides; the caesium distribution coefficient is always higher than 10^3 [3-5]. These compounds also have good retention properties for other elements [6, 7] and offer a very favourable procedure for recovering silver from dilute solutions [8, 9].

A very important point is the preparation of products usable as ion exchangers. Exchange capacities depend strongly on the composition of the ferrocyanide [10] as well as on the preparation conditions, and differ sometimes from batch to batch. Materials obtained by classical precipitation are generally fragile and require a solid support when used on columns [11]. Some authors have mixed the ferrocyanides with silica as a neutral support [12] or precipitated the nickel or zinc salt with chromatographic silica gel impregnated by potassium ferrocyanide [13]. Another approach was taken in [14] - zinc ferrocyanide was mixed with an organic polymer or synthetic organic resin. A nickel ferrocyanide was prepared inside the cavities of a macroreticular anion-exchange resin [15]. In order to overcome the poor mechanical properties of titanium ferrocyanide, this product was implanted into a matrix of a cation exchange resin [16-18]. These procedures cannot avoid a certain dilution of the sorbing material, accompanied quite often by a partial deterioration of its sorption properties.

The preparation of regular spheres from some insoluble ferrocyanides without any carrier is possible by the sol-gel method [19-21]. Unfortunately, bivalent

ions such as copper, nickel, cobalt or zinc which form the most efficient products [1, 2, 22] cannot at present be used for direct gelation [19]. On the other hand, a limiting factor in the use of zirconium, titanium or tin ferrocyanides, which can be prepared by the sol-gel method, is their higher solubility in water and their lower affinities towards caesium [2, 16]. The development of the use of ferrocyanides will lead to the preparation at low cost of a product with large, stable particles, which could be used under industrial conditions.

We have observed that alkaline ferrocyanide crystals (sodium or potassium), whose solubility in water is, respectively, 320 or 280 g l^{-1} , are insoluble in saturated zinc or nickel salt solutions. On the contrary, nickel or zinc salt crystals are soluble in saturated alkaline ferrocyanide solutions and precipitation of very small insoluble ferrocyanide particles occurs immediately.

After these observations, we have proposed a new preparation process by a method of growth from the solid [23]. The principle is slow growth of an insoluble compound on a soluble reacting crystal placed in a concentrated solution of another reactant. When an alkaline ferrocyanide $\text{M}_4\text{Fe}(\text{CN})_6$ crystal is placed in a solution of a metallic salt whose ferrocyanide complex is insoluble, a layer of this compound appears on the surface of the alkaline ferrocyanide and increases with a concomitant passage of the alkaline ion M^I in the solution. Here we present a detailed study of this method and a check that the product characterization fits the requirements for column utilization. This was performed through the search for the best experimental conditions connected with the control of particle

TABLE I Preparation conditions of nickel ferrocyanides

	Concentration (g l ⁻¹) Ni(NO ₃) ₂ · 6H ₂ O		Temperature (°C)	Yield* (%)	Remarks
	Initial	Final			
1	300 [†]	–	Room	–	No reaction
2	150 [†]	–	Room	50	–
3	120 [†]	–	Room	50	–
4	60 [†]	–	Room	< 5	Precipitation
5	300 [†]	150	Room	63	–
6	300 [†]	120	Room	80	–
7	300 [†]	90	Room	41	–
8	200	100	Room	< 5	Precipitation
9	240	–	Room	75	–
10	300	200	Room	80	–
11	300	240	37	100	–
12	300	–	45	90	–
13	600	–	50	95	–
14	1000	–	65	–	No reaction

*Yield for particle size > 100 μm.

[†] Solution containing also sodium nitrate (100 g l⁻¹).

size involving the use of different methods – radioactive tracers, potentiometric measurements, X-ray diffraction, optical and electron microscopy.

2. Experimental procedure

2.1. Preparation

All products used for preparations were from Prolabo, France. Sodium and potassium ferrocyanides were sieved and particles with sizes between 100 and 200 μm were used, if not otherwise specified. The main preparation conditions are summarized in Table I for nickel ferrocyanide and Table II for zinc ferrocyanide. We used two preparation procedures:

1. 1 g of alkaline ferrocyanide is introduced in 100 ml of a solution of nickel or zinc nitrate (Fig. 1). The weight of alkaline ferrocyanide was chosen to give a single layer of particles at the bottom of the vessel of diameter ~ 10 cm. The solution is slowly stirred (40 r.p.m.) in order to homogenize the solution, but

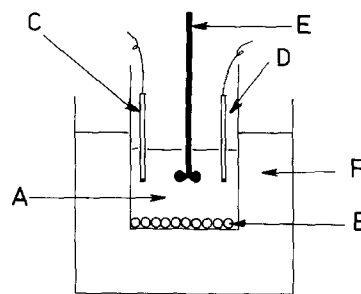


Figure 1 Scheme of the apparatus used for preparation of insoluble ferrocyanides by growth on alkaline ferrocyanide crystals by procedure 1. A, nickel or zinc salt solution; B, sodium ferrocyanide crystals; C, D, sodium specific electrode and reference electrode; E, stirrer, F, thermostated water bath.

not to move the solid particles. The quantity of sodium ions passing in the solution was measured by a specific electrode and by radioactive tracers. In the first step of the preparation, the alkaline ferrocyanide particles are covered by an insoluble layer whose thickness increases with time and then reaches a limit value. At the same time, the initial particle diameter decreases until complete disappearance. The experiment is stopped when the concentration of alkaline ions in the solution achieves a constant value. The required time varies between 1 h and a few days, depending on concentration and temperature.

2. A larger weight of alkaline ferrocyanide particles (10 g or more) is introduced in the apparatus of Fig. 2. These particles form a bed on the sintered glass filter (D in the figure). In order to homogenize the solution of nickel or zinc nitrate, but not to stir the solid, this solution is recycled at about 10 ml min⁻¹ through the bed, using peristaltic pumping (P₁ in the figure). In some cases, after about 1 h of contact, water was added in the solution using a second peristaltic pump P₂ (addition rate 0.2 to 1 ml min⁻¹). In other cases, the temperature was simply raised without diluting the

TABLE II Preparation conditions of zinc ferrocyanides

Starting products*	Divalent salt concentration (g/l)		Temperature (°C)	Yield [†] (%)	Remarks
	Initial	Final			
1 Na-N	120	–	Room	< 5	Precipitation
2 Na-N	150	–	Room	50	–
3 Na-N	200	–	Room	50	–
4 Na-N	300	–	Room	–	No reaction
5 Na-N	200	170	Room	85	–
6 Na-N	300	150	Room	66	–
7 Na-S	400	250	Room	30	Partial reaction
8 Na-S	500	360	Room	57	–
9 Na-N	300 [‡]	–	10	< 5	Precipitation
10 Na-N	300	–	40	100	–
11 Na-N	600	–	50–55	100	–
12 Na-N	600	–	65	88	§
13 K-N	180 [‡]	–	Room	< 5	No reaction
14 K-N	600 [‡]	–	Room	< 5	Precipitation
15 K-N	350	–	46	100	§
16 K-N	400	–	60	100	§
17 K-N	600	360	60	91	–
18 K-N	600	–	65	100	–

*Na : Na₄Fe(CN)₆·10H₂O; K : K₄Fe(CN)₆·3H₂O; N : Zn(NO₃)₂·6H₂O; S : ZnSO₄·7H₂O.

[†]Yield for particle size > 100 μm.

[‡]1 N HCl solution.

§Initial atomic ratio Zn_{solution} : Fe_{solid} = 2.

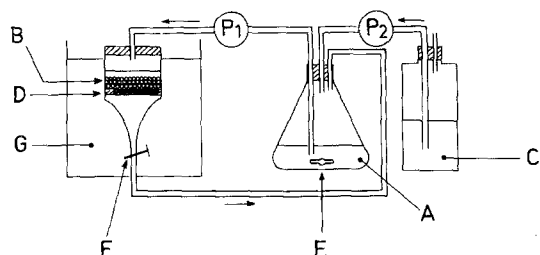


Figure 2 Scheme of the apparatus used for preparation of insoluble ferrocyanides by growth on alkaline ferrocyanide crystals by procedure 2. A, nickel or zinc salt solution; B, sodium ferrocyanide crystals; C, water; D, sintered glass; E, magnetic stirrer; F, tap; G, thermostated water bath; P₁, P₂, peristaltic pumps.

solution. The passage of sodium ions in the solution was measured as previously. The evolution of the solid was analogous. In both procedures the formed solid was separated from the liquid by filtration on a sintered glass filter (15 μm pore diameter). The solid was dried at 40°C for about 20 h, washed with water and dried again.

2.2. Potentiometric measurements

The release of Na⁺ ions in the solution was measured with a sodium-specific electrode coupled to an automatic burette (DL40RC METTLER Memotitrator) and connected to an Apple IIe microcomputer. The potential values can be registered every 5 sec. The validity of the calibration will be discussed elsewhere [24].

2.3. Radioactive tracers

Labelled ²⁴Na₄⁵⁹Fe(CN)₆ was produced by neutron activation of 1 g sodium ferrocyanide in a thermal neutron flux of 10¹³ to 10¹⁴ cm⁻² sec⁻¹ of the Saclay's reactors (Osiris or Orphee) using the facilities of the Pierre Sue Laboratory. Radioactive measurements were performed on a 3 × 4" NaI(Tl) detector coupled to a 400 channel analyser. The validity of the sodium-specific electrode response was controlled when using a labelled ferrocyanide by radioactivity measurements of an aliquot of the solution.

2.4. Analysis

Using the irradiation facilities of the Pierre Sue Laboratory, we performed non-destructive neutron activation analysis for the determination of sodium, potassium, nickel, zinc and iron. The sodium content was also deduced during the preparation from its release in the solution at equilibrium. The global yield of the preparation was deduced from the ⁵⁹Fe radioactivity measurements.

2.5. Granulometry and morphology

The granulometric distribution of the prepared particles was determined by sieving in water. Stainless steel sieves of 25, 75, 100, 200 and 500 μm were used. The particle morphology was determined by observations with a binocular optical microscope and a scanning electron microscope (SEM).

2.6. Endurance and stability tests

Water was poured on a column of ferrocyanide (inter-

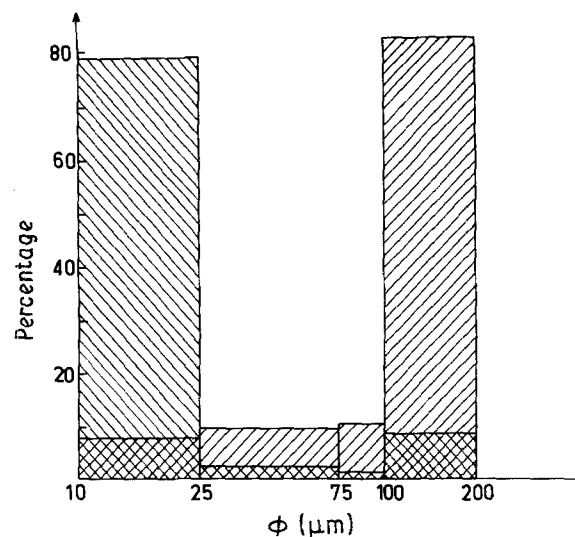


Figure 3 Distribution of particle sizes for nickel ferrocyanide prepared by growth on sodium ferrocyanide crystals ▨ and by classical precipitation ▩ .

nal diameter 1.8 cm; height 40 cm; height of product 4.5 cm; product weight 10 g) and recycled for 10 days with a hydrostatic pressure of ~40 cm. Experiments were performed at room temperature and at 40°C. The increase of pressure was quoted as a function of time [25].

The release of cations in the solution was controlled after passage of water or lithium borate solutions on columns. The main cations of the product in the solutions were checked by atomic absorption [4].

2.7. Exchange properties

The exchange properties were studied on columns of ferrocyanides using ¹³⁷Cs and ^{110m}Ag isotopes as described elsewhere [3, 6, 8, 25].

3. Results and discussion

The yields for various conditions are given in Table I for nickel ferrocyanides and in Table II for zinc ferrocyanides. Starting from solid crystals whose size is over 100 μm , if the required conditions of temperature and concentration are fulfilled, this method allows the preparation with a good yield of particles whose dimensions are suitable for column utilization. For example, 100 μm large beads of mixed potassium-zinc ferrocyanide can be produced by this method. These yields have never been reached by classical precipitation methods [11, 26]. An example of particle-size distribution is given in Fig. 3 for both types of preparation.

3.1. Determination of the preparation conditions

We have successfully used sulphate or nitrate salts for preparation. However, we have studied in more detail preparations with nitrate salts, which can be used over a wider range of concentrations owing to their higher solubility. To a certain extent, sodium does not interfere with the preparation (see Table I), which means that solutions can be re-used.

3.1.1. Influence of the salt concentration

Figure 4 shows the influence of dilution on the evolu-

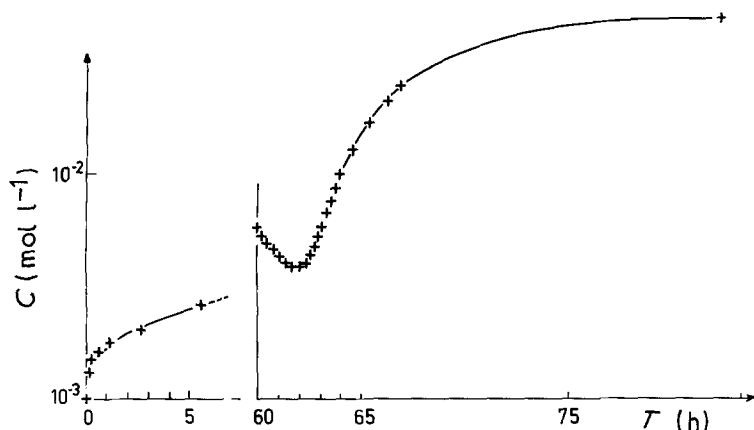


Figure 4 Variation of the released sodium concentration C as a function of time T from 10 g sodium ferrocyanide crystals placed in 100 cm^3 of nickel nitrate solution (300 g l^{-1}) at room temperature. After 60 h, 25 cm^3 of water are added.

tion of sodium concentration in the solution. When sodium ferrocyanide crystals are placed in a concentrated nickel solution ($300\text{ g l}^{-1}\text{ Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) at room temperature, a small quantity of sodium appears in the solution, but the increase in concentration slows rapidly and after 60 h of contact, the sodium release remains inferior to 5% of the starting sodium content of the ferrocyanide. The crystals are covered with a thin film whose thickness grows very slowly. When water is poured into the solution, a normal decrease in sodium concentration takes place until a critical concentration of the divalent salt is reached. For a certain dilution, the sodium concentration starts to rise. At equilibrium, it corresponds to 80% of the content of the starting solid. After sieving and washing, the product does not include soluble ferrocyanide; it is composed of small hollow beads whose diameter is slightly larger than $100\text{ }\mu\text{m}$ (Fig. 5).

The salt concentration is very important for this method. If the dilution is too high, alkaline ferrocyanide is soluble and precipitation takes place in the whole volume of the solution. If the concentration exceeds the required value, the surface layer does not change any more and the reaction is stopped. Unreacted alkaline ferrocyanide remains inside the particle. The formation and thickness of the insoluble ferrocyanide superficial layer depend on the experimental conditions. At room temperature, a yield greater than 50% for particle size over $100\text{ }\mu\text{m}$ is

obtained for concentrations of divalent salt of 120 to 240 g l^{-1} , the best ones corresponding to 200 to 240 g l^{-1} . We have followed the sodium concentration in the solution as a function of time for various nickel or zinc concentrations between the required limits. The lower the starting concentration, the faster the sodium concentration increases in the solution. In Fig. 6 we show some results for zinc solutions.

3.1.2. Influence of the temperature

The increase of temperature has an effect similar to dilution. Figure 7 shows the reaction kinetics for sodium ferrocyanide crystals placed in a 0.8 M nickel nitrate solution at various temperatures. The higher the temperature the faster the sodium concentration increases in the solution.

3.2. Morphology

Particles prepared by growth on alkaline ferrocyanide are constituted of hollow spheres (Fig. 5). SEM observations show a matrix with no discernable grains (Fig. 8).

The particle size is related to the granulometry of the starting alkaline ferrocyanide, as well as to the solution concentration and temperature — it increases with temperature and dilution. For low divalent metal concentrations we obtain larger particle sizes but these particles are fragile and break during sieving. The fraction of sieved particles whose diameter exceeds

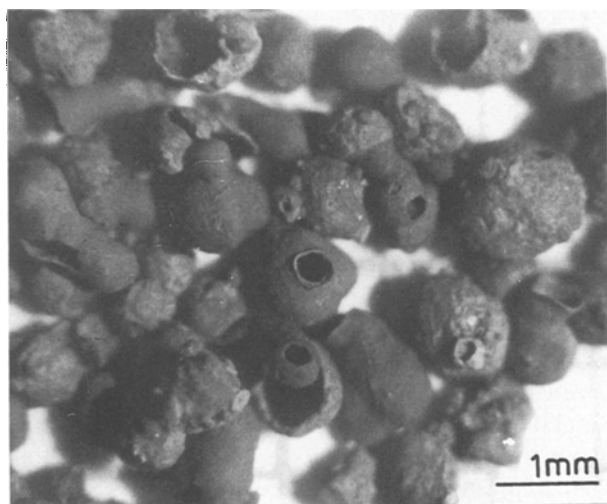


Figure 5 Micrograph of a nickel ferrocyanide prepared by growth on sodium ferrocyanide crystals.

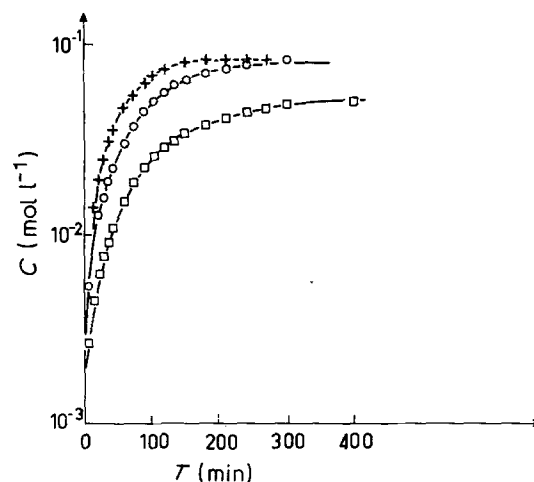


Figure 6 Variation of the released sodium concentration C as a function of time T from 1 g sodium ferrocyanide crystals placed in 100 cm^3 of a zinc nitrate solution at 46°C for various zinc nitrate concentrations. \square , 1.2 M ; \circ , 1.0 M ; $+$, 1.08 M .

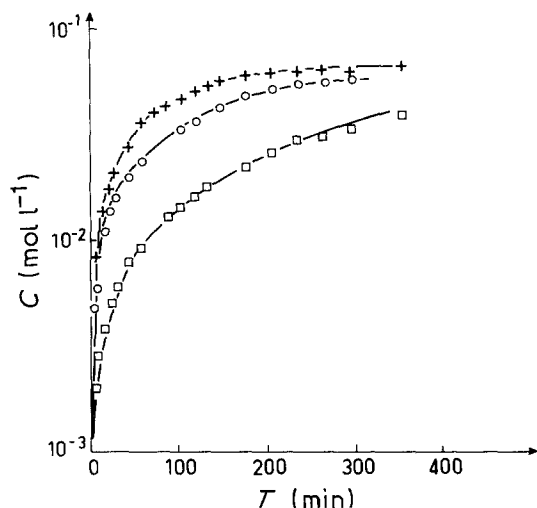


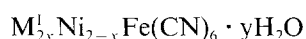
Figure 7 Variation of the released sodium concentration C as a function of time T from 1 g sodium ferrocyanide crystals placed in 100 cm^3 of a 0.8 M nickel nitrate solution at various temperatures. \square , 27°C; \circ , 37°C, +, 46°C.

$100\ \mu\text{m}$ is low. For concentrations lower than $100\ \text{g l}^{-1}$, the bead formed by dissolution of the alkaline ferrocyanide grows too fast and bursts like a soap bubble. Precipitation occurs immediately.

The best yields obtained correspond to particles whose diameters are 20% larger than those of the starting alkaline ferrocyanide particles. For starting particles larger than $100\ \mu\text{m}$, we observed 90 to 100% of particles with the same size range.

3.3. Composition and structure

Some examples of compositions for products prepared by this method are given in Table III. They correspond to several types of formula and structure. Nickel ferrocyanides can be represented by the general formula



where M^{I} is hydrogen or sodium. The value of x varies in a large range. All the X-ray diagrams can be indexed by a fcc structure. Sodium zinc ferrocyanides present a mixture of phases. According to preparation conditions, the main phase may be $\text{Na}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 \cdot x\text{H}_2\text{O}$ (rhombohedral) or $\text{Zn}_2\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$ (trigonal). Starting from potassium ferrocyanide, the rhombohedral phase $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 \cdot x\text{H}_2\text{O}$ is always obtained.

3.4. Mechanical resistance

Mechanical resistance depends on the increase of par-

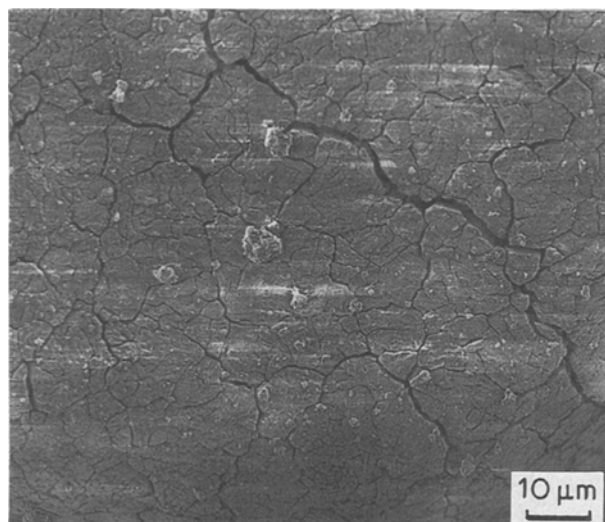


Figure 8 Scanning electron micrograph of a zinc-sodium ferrocyanide prepared by growth on sodium ferrocyanide crystals.

ticle size during preparation (see Table IV). If the diameters of the final beads exceed too much the size of the starting ferrocyanide crystals, they are not mechanically resistant and break into fine particles during sieving. If the size increase is about 40%, they split into a few pieces which are suitable for utilization. The best results correspond to particles whose sizes increase less than 20% — in this case, the hole in the middle of the particle is minimal.

The stability of particles put in chromatographic columns was tested. Large volumes of water were passed through columns loaded with ferrocyanides at a constant flow rate and the applied pressure measured as a function of time. As an example, the mechanical resistance of a 10 ml zinc-potassium ferrocyanide column was sufficient for processing a solution of 20 000 column volumes without any significant increase of the pressure.

3.5. Chemical stability

Stability was tested in a variety of solutions. Zinc ferrocyanides can be used from pH 1 to 10, nickel ferrocyanides from pH 0 to 12. Most anions do not affect the product, except complexing agents such as cyanides. Organic solvents such as alcohols and acetone can be used. These products were tested between 20 and 60°C.

In some experiments on columns, the quantities of

TABLE III Compositions* and structure of some products

Number [†]	Zinc	Nickel	Sodium	Potassium	Hydrogen	H ₂ O	Structures [‡]
2	1.86	—	0.94	—	—	?	Rhombohedral
6	1.46	—	0.40	—	?	?	Rhombohedral
11	1.89	—	0.10	—	—	7	Trigonal
15	1.60	—	0.03	0.96	—	3.4	Rhombohedral
3	—	1.56	0.91	—	—	8.8	fcc
5	—	1.15	1.35	—	—	5.1	fcc
11	—	1.33	1.78	0.04	—	11	fcc
12	—	1.21	1.75	—	—	4.8	fcc

*Composition of the products in atoms per one iron atom.

[†]Preparation conditions are given under the corresponding number in Table I for nickel ferrocyanides and Table II for zinc ferrocyanides.

[‡]main structure observed.

TABLE IV Particle sizes and mechanical resistance of some zinc ferrocyanides*

Zn(NO ₃) ₂ ·6H ₂ O (mol l ⁻¹)	Temperature (°C)	Mean size (μm)	Mechanical Resistance
0.8	46	580	Bad
1	46	490	Medium
1.2	46	370	Very good
0.5	37	570	Bad
0.8	37	480	Medium
1	37	430	Good

*Mean particle size of the starting sodium ferrocyanide, 350 μm.

elements released from the solid into the solution were measured. After passage of about 40 l of demineralized water on 7 g of potassium zinc ferrocyanide, the mean release is about 3 mg l⁻¹ for zinc and 2 mg l⁻¹ for potassium. The release of iron is negligible. The release of alkaline ions can be easily explained by the exchange with the H⁺ ions of the solution. The presence of zinc ions cannot be explained by the solubility product of the solid. However, a slight decomposition of the product connected with prussian blue formation is possible. At the present time, the release of cations is the most limiting factor in the use of ferrocyanides for the decontamination of the primary circuit of PWR reactors from caesium and silver [25, 27].

3.6. Exchange properties

Measurements of distribution coefficients and retention capacity for caesium and silver were performed on products prepared by this new method, and compared with results obtained on normally precipitated ferrocyanides. We did not detect any difference in the results. The products prepared by the new method are highly attractive for Cs⁺ and Ag⁺ fixation from solutions [25, 27].

4. Conclusions

Nickel and zinc ferrocyanides have the advantage of all inorganic fixators in being radiation resistant and chemically stable in a large pH range and in various solvents. The use of such products was limited by the particle size obtained by classical methods. This difficulty was overcome by a new preparation method in which the particle size can be easily controlled. This method is based on the slow growth on solid alkaline ferrocyanide particles placed in a concentrated nickel or zinc salt solution. The phenomena governing this method are under investigation. It seems that the first step is the formation of a thin film of insoluble ferrocyanide on the surface of alkaline ferrocyanide, thus preventing the rapid dissolution of this salt and precipitation in the whole volume of the solution. Film growth seems to be controlled by diffusion of water and cations through the solution. Temperature increases the growth kinetics as usual. On the other hand, the concentration of the divalent salt has an unusual effect — the higher this concentration, the slower the kinetics. At present, the conditions leading to controlled size and stability are well established for nickel and zinc ferrocyanides at the laboratory scale. Owing to the relatively simple method of prepara-

tion, it is thought that larger scale manufacture would be feasible and economical. This type of compound can be used for the decontamination of caesium from radioactive waste. ¹³⁷Cs has a commercial value as a source for irradiation and for density detectors, and can be recovered for such purposes on ferrocyanide columns. We are also studying the extension of this method of preparation to other insoluble compounds.

References

- G. B. BARTON, J. L. HEPWORTH, E. D. McCLANAHAN Jr, R. L. MOORE and H. H. VAN TUYL, *Ind. Eng. Chem.* **102** (1958) 212.
- H. LOEWENSCHUSS, *Radioact. Waste Manag.* **2** (1982) 327.
- C. LOOS-NESKOVIC, PhD thesis, Paris (1986).
- C. LOOS-NESKOVIC and M. FEDOROFF, *Solvent Extr. Ion Exch.* **7** (1989) 131.
- Idem*, *React. Polym.* **7** (1988) 173.
- C. LOOS-NESKOVIC, M. FEDOROFF and G. REVEL, *J. Radioanal. Nucl. Chem.* **30** (1976) 533.
- M. T. GANZERLI-VALENTINI, S. MELONI and V. MAXIA, *J. Inorg. Nucl. Chem.* **34** (1972) 1427.
- M. FEDOROFF and C. LOOS-NESKOVIC, *Mater. Tech.* (1982) 357.
- C. LOOS-NESKOVIC and M. FEDOROFF, *Ann. Chim. Fr.* **9** (1984) 609.
- S. KAWAMURA, H. KURAKU and K. KUROTAKI, *Anal. Chim. Acta* **49** (1970) 317.
- C. LOOS-NESKOVIC, M. FEDOROFF, E. GARNIER and P. GRAVEREAU, *Talanta* **31** (1984) 1133.
- S. VLASSELAER, W. D'OLIESLAGER and M. D'HONT, *J. Inorg. Nucl. Chem.* **38** (1976) 327.
- C. KONECNY and R. CALETKA, *J. Radioanal. Chem.* **14** (1973) 255.
- J. STĚJSKAL, J. SOUKUP, J. DOLEZAL and V. KOURIM, *ibid.* **21** (1974) 371.
- K. WATARI, K. IMAI and M. IZAWA, *J. Nucl. Sci. Tech.* **6** (1969) 522.
- J. NARBUTT, J. SIWINSKI, B. BARTOS and A. BILEWICZ, *J. Radioanal. Nucl. Chem.* **101** (1986) 41.
- J. NARBUTT, A. BILEWICZ and E. GNIAZDOWSKA-LAREN, in International Symposium on Water Chemistry Corrosion Problems, Vienna, Austria, November 1982 (IAEA-SM-264/31; 1983) p. 287.
- A. BILEWICZ and J. NARBUTT, *Isotopenpraxis* **20** (1984) 141.
- V. BARAN, R. CALETKA, M. TYMPL and V. URBAŃEK, *J. Radioanal. Chem.* **24** (1975) 353.
- L. M. SHARIGIN, V. E. MOISSEV, R. V. KUZ'MINA, YO. V. EGOROV, V. P. PISHKIN, S. P. KURUSHIN and V. M. GALKIN, *Radiokhim.* **28** (1986) 361.
- A. G. VISZHATCHIL, V. E. MOISSEV and L. M. SHARIGIN, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **22** (1986) 460.
- W. F. HENDRICKSON and G. K. RIEL, *Health Physics* **28** (1975) 17.
- M. FEDOROFF and C. LOOS-NESKOVIC, French Patent 84-12139 (1984).
- C. LOOS-NESKOVIC, S. ABOUSAHL and M. FEDOROFF, *The Analyst*, to be published.
- C. LOOS-NESKOVIC and M. FEDOROFF, *Radioactive Waste Manag.* **11** (1989) 43.
- C. LOOS-NESKOVIC, M. FEDOROFF and E. GARNIER, *Talanta* **36** (1989) 749.
- C. LOOS-NESKOVIC, M. FEDOROFF, M. LE VERRE and J. RUEL, Proceedings of the Symposium in Waste Management, Tucson, Arizona, USA, 15 March, 1987, Vol. I (1987) p. 563.

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