A NEW ALTERNATIVE FOR THE DECONTAMINATION OF PWR PRIMARY CIRCUITS FOR RADIOACTIVE CESIUM AND SILVER BY INSOLUBLE FERROCYANIDES

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ABSTRACT

The optimal recovery conditions of radioactive cesium and silver from PWR primary circuits were determined on two types of nickel and zinc ferrocyanides. The studied products have been prepared by a slow growth on solid alkaline ferrocyanide particules placed in a concentrated nickel or zinc salt solution. Columns of these products do not react with water or lithium borate solutions as well as with organic solvents. The decontamination factor for cesium or silver is over 1000 for sythetic solutions. The presence of other alkaline ions does not modify these results. In the case of nuclear liquid wastes, the decontamination remains high for cesium. Silver is retained with a good efficiency if it is not under a complex form. This complex is destroyed by acidification. The setting of concrete is not significantly modified by the presence of ferrocyanides. The drawback of this method is a slight elution of some cations composing the ferrocyanides.

INTRODUCTION

The management of radioactive wastes has become a major concern, particularly with regard to the release of radioactive materials to the environment. At present time, PWR primary circuits are decontaminated by organic resins. Purification of the long lived radioactive nuclides ^{110m}Ag and ^{137}Cs creates some problems due to the rather low affinity of conventional demineralizers for these ions under normal PWR conditions (1). Typical values of the radioactivity during normal operation are 2 to 3 microCi/l for ^{137}Cs (2). Decontamination is especially difficult in the case of boric acid solutions buffered by potassium, lithium and ammonium hydroxides, these cations being strongly competitive with cesium for sites in the ion exchangers. Moreover, organic resin beds are not radiation or high temperature resistant and cannot be directly wrapped by concrete for final disposal.

Inorganic fixators, especially insoluble ferrocyanides, seem to be promising for such decontamination (3-8). We have studied the fixation mechanisms of cesium and silver on nickel and zinc ferrocyanides (9-13). The selection of a particular ion exchanger is not only governed by its capacity and selectivity for the species to be removed from the chemical content of a particular waste, but also by considerations on availability in a reproducible form, handling characteristics, suitability for elution operations and potential for immobilization. Recently, we have proposed a new preparation process which controls the particle size and produces ferrocyanides suitable for use on columns (14). A recent US patent (15) claims that ^{137}Cs loaded cyanoferrates can be immobilized by incorporation into glass containing 10 to 30 weight percent of cyanoferrates.

Owing to the support of our anterior studies, this work was devoted to the determination of the optimal recovery conditions of radioactive cesium and silver from PWR primary circuit on several types of nickel and zinc ferrocyanides. Laboratory-scale studies were undertaken in order to propose an additional demineralizer highly selective for these elements.

MATERIALS

Nickel and zinc ferrocyanides have been prepared by various ways. For fundamental studies, they have been precipitated directly by mixture of solutions containing ferrocyanide anions and zinc or nickel salts. Pure and mixed zinc ferrocyanides were prepared according to literature recommendations (16, 17). We have tested in addition other procedures: direct precipitation with sodium or potassium ferrocyanide and various Za:Fe or Ni:Fe ratios or precipitation with ferrocyanhydric acid obtained by exchange on a cationic resin, in presence or not of an alkaline salt (Na^+, K^+, NH_4^+) (12). For column studies, the products were prepared by slow growth on sodium or potassium ferrocyanide crystals placed in a concentrated nickel or zinc salt solution (14). All products were analysed for their composition by non-destructive neutron activation analysis, atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry and complexometry.

If prepared by precipitation, the particle size of the products varies according to the presence or not of an alkaline ion and according to the monovalent cation present in the precipitate in the following the order:

$$\text{none},\ H^+ > NH^{4+},\ Na^+ > K^+$$

Only the products without alkaline ions include a sufficient fraction of large particles. The preparation proposed in (14) leads with a high yield to ferrocyanides directly suitable for column utilizations.

Nickel ferrocyanides can be represented by the general formula $M^I 2xNi2\text{-}xFe(CN)_6$, YH_2O where M^I is H, NH_4, Na or K. In some cases we have a mixture of H with an alkaline element. The value of x varies between 0.2 and 1. All the x-ray diagrams of these products can be indexed by a f.c.c. structure with a mean parameter of 10.2 A per unit-cell.

Compositions close to definite formulae were obtained for all single-phased zinc ferrocyanides. The mixed ferrocyanides belong to the $M^1$2Zn3/Fe(CN)6/2 series (M^1 = H, Na, K) with a rhombohedric structure R3C (18). Pure zinc ferrocyanide has a Zn2Fe(CN6, 2H2O composition and a trigonal structure similar to the product of Siebert (19). The mixed sodium zinc ferrocyanides obtained by slow growth on sodium ferrocyanide differ from batch to batch. According to the preparation conditions, (temperature, zinc concentration of the solution), the product may be pure zinc ferrocyanide with a trigonal or a cubic structure already pointed out by Garnier (18), or rhombohedric sodium zinc ferrocyanide, or a mixture of different phases. Mixed potassium zinc ferrocyanides obtained in a similar way do not differ much in composition and their structure is rhombohedric.

Photographs obtained by electron microscopy show that the directly precipitated products are composed of small crystals, whose dimensions are smaller in the case of nickel ferrocyanide (mean grain diameter: 0.06 μm). The dimensions of the crystals of zinc ferrocyanide are about 0.2 μm (13). The adsorption and desorption isotherms obtained for zinc, zinc-sodium and nickel-sodium ferrocyanides are similar to molecular sieve 4A. The macroscopic porosity of the products seems to be of the same order of magnitude and the specific surfaces range from 30 to 75 $m^2 \cdot g^{-1}$ (12).

Products prepared by slow growth on alkaline ferrocyanides (14) are constituted of hallow spheres (Fig. 1.). The diameter of these spheres is related to the diameter of the crystals used as starting products. It is easy to obtain particles between 100 and 500 μm. The sweeping electron microscope shows a matrix with no detectable particles supporting some crystals.

STATIC STUDIES

25 cm^3 of a solution containing various silver or cesium quantities and labelled with ^{110m}Ag or ^{134}Cs were added to 100 mg of ferrocyanide. After a required time of shaking, the solution was filtered and the radioactivity of 10 cm^3 measured and referred to the amount of the product (Fe, Ni, Zn, Na, K) were determined by atomic absorption spectrometry.

Silver Fixation

For small silver quantities, when the atomic ratio of silver in solution to iron in the product is inferior to 0.05, the fixation is achieved within a few minutes. For quantities reaching several silver atoms per iron atom, the reaction is completely performed within an hour, whatever the composition of the ferrocyanide is. The capacity of the various products towards silver is always very high. The main feature is a substitution of all ferrocyanide cations by silver. But the capacity frequently exceeds the value of four silver atom per iron predicted by the possible formation of silver ferrocyanide. In the first step of silver fixation (atomic ratio Ag: Fe <1), the exchange balance of the various cations has shown that a preferential release is noticeable in the order: Na> Zn> H> Cs for zince ferrocyanides and Na, K> H,NH^+_4> Ni for nickel ferrocyanides. Silver fixation leads to a structural change for zinc ferrocyanides with the exception of sodium zinc ferrocyanide retaining silver in neutral medium without modification of the structure for Ag : Fe < 0.8. There is no obvious structural change on nickel ferrocyanides. However, even in this case, the fixation seems irreversible.

Fig. 1. Micrograph of a nickel ferrocyanide prepared by slow growth on sodium ferrocyanide crystals (magnification X 15).

Cesium Fixation

In a concentrated cesium solution, sorption rate on pure zinc ferrocyanide is extremely slow (17), while cesium is retained on mixed zinc and nickel ferrocyanides within ten minutes. The maximal observed capacities in neutral medium are respectively 1.65, 0.9, 0.71 cesium atoms per iron atom in the solid for pure zinc, sodium or potassium zinc and sodium nickel ferrocyanides. The capacities do not decrease in acidic solutions and even increase for nickel ferrocyanide until 0.94 cesium atom in a 0.1 M hydrochloric solution. Similar results are obtained whatever the preparation mode is. Starting from Ms2Zn3/Fe(CN)6/2, we obtained a composition close to Cs2Zn3/Fe(CN)6/2 without structural change. The fixation on nickel ferrocyanides takes place without changing the crystal structure. From Zn2Fe(CN)6, we achieved a Cs1.3Zn1.35/Fe(CN)6/2 composition departing from the reported Cs2ZnFe(CN)6 (20, 21). X-ray diffraction patterns showed a mixture of two cubic phases: Cs2ZnFe(CN)6 and Zn2Fe(CN)6 (18, 22). In the case of mixed ferrocyanides, nickel or zinc were never found in the solution and the release of alkaline ions explains the fexation, which is in agreement with an hypothesis of pure exchange process (23). On pure zinc ferrocyanide, the uptake of cesium is not only explained by the exchange, but partly by adsorption of CsCl (12, 13).

DYNAMIC STUDIES

Dynamic fixation of cations was studied by pouring solutions through a column of ferrocyanide. In a first set of experiments, we used small columns containing about 1g of product (diameter 0.7 cm, height 3cm, flow rate from 0.5 to 6 ml/mn). In further experiments, the dimensions of columns were enlarged. The decontamination factor is defined as the ratio of the radioactivities of the solution before and after passage through the column.

Silver

Owing to the affinity of silver ions for ferrocyanides, the decontamination factor remains very high even close to the saturation of the column. On nickel-potassium ferrocyanide, it is over 1000 as long as the capacity of 1 g/g is not reached with flow rates up to 15 cm^3, cm^{-2}, min^{-1}. The ferrocyanides can be used on a large range of pH (1-11) without any influence on the retention. Among the various ions retained on ferrocyanide columns (9), only a very few, such as iron, forming insoluble ferrocyanides with solubility products of the same order of magnitude as silver, interfer. They lower the capacity of the products but do not act on the decontamination factor. Silver ions are not retained if they are in the solution under a complex form: silver cyanide, thiocyanate, thiosulfate or sulfide for example. Ammonium acting as a complexing reagent in basic medium avoids the fixation of silver, but does not interfer in acidic solutions when the complex is destroyed (10). Zinc ferrocyanides cannot be used for the fixation of large quantities of silver, because the fixation of this element is accompanied by a destruction of the initial structure and the columns clog rapidly, but for traces their efficiency is equivalent to nickel ferrocyanides (12, 24).

Cesium

We give in Table I the experimental results of cesium fixation from water solutions poured on columns of various ferrocyanides prepared by slow growth on the solid.

Owing to its slow kinetics of fixation, pure zinc ferrocyanide gives pour results and must be discarded. For the other products, the decontamination factor does not vary until the cesium quantity retained on the column reaches the working capacity and then drops abruptly. However, it seems that the best is $K_2Zn_3/Fe(CN)_6/_2$. Its working capacity reaches 90% of the theoretical capacity corresponding to one atom of cesium for each iron atom of the ferrocyanide. The retention properties are unaffected when the pH of the solution varies and the decontamination factors are even higher in acidic medium.

TABLE I

Retention of Cesium on Some Zinc and Nickel Ferrocyanides[1]

Product	D[2]	Cw[3]	Cmax[4]
$Zn_2Fe(CN)_6.2H_2O$	10	0	0.32
$Na_2Zn_3/Fe(CN)_6/_2.xH_2O$	1000	0.27	0.29
$K_2Zn_3/Fe(CN)_6/_2.xH_2O$	>3000	0.27	0.32
$Ni_{1.5}Na_{1.7}Fe(CN)_6.xH_2O$	1000	0.12	0.18

1. Polyethylene columns loaded with 1 g of product; solution flow rate: 2 to 5 $cm^3.cm^{-2}.min^{-1}$.
2. Decontamination factor
3. Working capacity: maximal uptake for a decontamination factor superior to 100, in g of cesium per g of product.
4. Total capacity in g of cesium per g of product.

PWR Effluents

We tested two types of water samples: effluents from the primary circuit of a reactor or water from cooling pools. The pH of the various solutions was fixed to 7 by the presence of large quantities of lithium borate (7 g/l). The radioisotopes found in both cases are globaly the same, but the radioactivity of the first samples is much higher; on the other hand, the presence of ^{110m}Ag is more obvious in the second samples owing to the lower activity of cesium.

The results are given in Table II and represent mean values on at least five different columns of each ferrocyanide and solution types. They are obtained on 1 g of product. We were surprised by the lack of reproducibility towards silver fixation. One possible explanation is the presence in certain cases of small amounts of ammonium ions due to the purification system of water before introduction in the reactor. This hypothesis is comforted by the good decontamination factors obtained in any cases if the solution is acidified by nitric acid (1 < pH < 2). The results towards cesium are not modified in this case. Apart from cesium and silver isotopes, cobalt, iron and zinc are retained on the columns. For example, on 10 g of mixed sodium zinc ferrocyanide, the decontamination factors observed on 100 cm^3 of primary effluent was superior to 100 for these elements.

TABLE II

Decontamination Factors Observed for Cesium and Silver on PWR Effluents

ferrocyanide	Cs	Ag	
cations		a	b
Ni-Na	60	2	>100
Zn-Na	60-600[c]	2	>100
Zn-K	>1000	2	250

a. Results obtained in the worst cases

b. Results obtained in the best cases or in acidic medium

c. Ferrocyanide weight: 10 g.

MECHANICAL AND CHEMICAL RESISTANCE

Mechanical Stability on Columns

The mechanical stability of ferrocyanides prepared by the slow growth method was tested by passing large volumes of solutions and measuring the evolution of the pressure applied to the column for a constant flow rate. As an example, a column of 10 ml zinc-potassium ferrocyanide (internal diameter: 1 cm) was treated by recycling a 30 l effluent solution from a PWR reactor. A flow rate of 15 solution volumes per column volume and per hour was maintained during 55 days without any significant increase of the pressure. The decontamination factor for cesium was always higher than 1000. So, the mechanical resistance of the particles was sufficient for processing a solution of 20,000 column volumes. In an other example, 100,000 column volumes were processed at a flow rate of 670 vol./vol.h. With such a high flow rate, the applied pressure varied from 20 to 25 Hg cm.

Chemical Stability

It was tested in a variety of solutions. Zinc ferrocyanides can be used from pH 1 to 10, nickel ferrocyanides from pH 0 to 11. 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^{0}C without any noticeable change of their properties.

In some experiments on columns, the quantities of elements released from the solid into the solution were measured. The release of alkaline ions can be easily explained by the exchange with the H^+ ions of the solution. We also observed zinc ions which cannot be explained by the solubility product of the solid. The release of iron is neglegible. At present time, the release of cations is the most limiting factor for using ferrocyanides on the primary circuit of PWR reactors.

Immobilization Into Concrete

Ion exhange resins cannot be directly immobilized into concrete because of swelling. This phenomenon does not exist with inorganic fixators. Some assays on the influence of the addition of ferrocyanides (1-2%) into concrete were performed. No effect was noticed on the time required for solidification, although zinc is known for its retarding effect. The strength of the concrete was not modified.

CONCLUSION

We have studied the fixation characteristics of cesium and silver on nickel and zinc ferrocyanides. They are especially good absorbers for these elements. We have determined the optimal recovery conditions from PWR primary circuits on several types of products. Until now, the use of inorganic fixators prepared by direct precipitation was limited, owing to their small praticle size resulting in clogging the columns. 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 particules placed in a concentrated nickel or zinc salt solution. The decontamination factor for cesium or silver is over 1000 for synthetic solutions; the capacity for silver is about 1 g and for cesium 0.3 g for 1 g of ferrocyanide. The presence of other alkaline ions does not modify these results. In the case of nuclear liquid wastes, the decontamination remains high for cesium. Silver is retained with a good efficiency if it is not under a complex form. This complex is destroyed by acidification. The setting of concrete is not significantly modified by the addition of 2% weight ferrocyanides. The drawback of this method is a slight elution of some cations composing the ferrocyanides. We are studying methods for reducing this release. For this reason, this type of compounds can be used for the decontamination of PWR liquid effluents before final disposal. Another application is the selective removal of radioactive cesium from ion exchange resins used in the purification circuits (25). A volume reduction factor superior to one order of magnitude can be achieved by transferring the activity from the resin onto a smaller volume of ferrocyanide.

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