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(54) **Method for removing cesium from aqueous solutions of high nitric acid concentration.**

(57) A method for removing cesium, e.g., radioactive nuclides of cesium, from an aqueous solution containing nitric acid in high concentration, such as a high-level radioactive waste solution from the Purex process, comprising sorption on an insoluble ferrocyanide compound as the sorbent, wherein the aqueous solution is mixed with a small amount of a specific oxidation-preventing agent selected from hydrazinium compounds, amidosulphonic acid compounds and several other compounds which do not necessarily have high reducing activity for ferricyanides into ferrocyanides.

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The present invention relates to a method for removing cesium from an aqueous solution containing nitric acid in a high concentration of, for example, 1M or higher. More particularly, the invention relates to a reliable and efficient method for removing cesium from an aqueous solution containing nitric acid in a high concentration by sorption on a solid sorbent. The method is of course applicable to the removal of radioactive nuclides of cesium from a high-level radioactive waste solution produced in facilities relative to atomic power plants such as a reprocessing plant for spent nuclear fuels.

As is known, the so-called purex process is and will be the major method for the reprocessing of spent nuclear fuels. The purex process necessarily produces a large volume of high-level radioactive waste solutions which are highly acidic since they contain nitric acid in a concentration as high as 2M to 4M. Accordingly, one of the most serious issues in completing a nuclear fuel cycle is to establish a reliable and efficient method for the disposal of such high-level radioactive waste solutions while each of the heretofore proposed methods therefor is defective in one or more respects.

One of the processes now under active development for the disposal of high-level radioactive waste solutions is to convert the solution as collected into a glassy or vitrified solid which is stored, for example, deep underground. This method, however, has the following problems. While the high-level radioactive waste solutions usually contain radioactive nuclides of cesium such as ^{137}Cs and ^{134}Cs each in a substantial concentration, for example, these radioactive nuclides of cesium have relatively high vaporizability so as to be readily dissipated into the atmosphere in the course of the vitrification treatment and causing serious radioactive contamination of the environment which can be prevented only with great difficulty. Further, various atomic species having radioactivity are soretimes subject to leaching out into underground water with which the glassy solid stored underground is contacted and it is a very difficult matter to completely prevent leaching-out of such radioactive species into water. The radioactive nuclides of cesium also belong to the class of the species having highest leachability. In addition, great difficulties are encountered in the safety assessment of this process in relation to the safety to be secured in handling and transportation as well as in the storage of the glassy solids due to their strong radioactivity and the large quantity of heat evolved therefrom.

Accordingly, it would not be unreasonable to expect that the problem of the disposal of high-level radioactive waste solutions could be partly, though not completely, solved when the waste solutions are subjected to a preliminary treatment for the removal of the radioactive nuclides of cesium and strontium since more than 90% of the radioactivity of waste solutions are ascribable to the radicactive nuclides of these two elements. Apart from the problem of safety in the disposal of radioactive waste solutions, moreover, a significant industrial advantage could be expected if the radioactive nuclides of these elements removed from waste solutions could be recovered. This matter is discussed, for example, in IAEA-SM-261/34, page 461 (1983) which includes discussion of methods for the preliminary removal of radio-active cesium and strontium from high-level radioactive waste solutions. In particular, radioactive cesium is important due to a growing demand for it as a gamma-ray irradiation source in the germicidal treatment of various kinds of foods as well as the excess sludge produced in the activated sludge process for the disposal of municipal sewages.

Since the gamma-radioactivity in high-level radioactive waste solutions is mostly ascribable to radioactive cesium, it is a very serious technical problem to develop and establish a reliable and efficient process for the removal of radioactive cesium from waste solutions because of the great reduction in costs expected for gamma-ray shielding in the treatment of the remaining portion of waste solutions and in the handling and transportation of canisters even if the radioactive nuclides of other elements are not removed, when the advantages to be obtained from the recovered radioactive cesium are additionally taken into consideration.

One of the most promising processes recently high-lighted for the disposal of high-level radioactive waste solutions is the so-called partitioning followed by transmutation in which the radioactive species in the waste solution are separated into groups and those belonging to the group having utilizability are recovered and utilized as a resource while those having no utilizability with a long half-life period are subjected to a treatment of transmutation so as to achieve final disposal of the waste solution with high safety. In this case also, preliminary removal of the radioactive cesium from the waste solution can be an important technological step since the major portion of the radioactivity therein is ascribable to radioactive cesium.

Various proposals and attempts have been made heretofore for the removal of radioactive cesium from high-level radioactive waste solutions including, among those now under development, adsorption methods by using an inorganic ion exchanger or a selective ion-exchange resin, solvent-extraction methods using a crown ether as the extractant, methods of coprecipitation by the combined use of a heavy metal salt and a water-soluble ferrocyanide or ferricyanide and chemical treatment methods using a precipitant reagent for cesium. In view of the relatively high decontamination factor, i.e. the ratio of the concentration of the radioactive species in the solution before treatment to that after treatment, as well as the high resistance of the material concerned to heat and radioactive irradiation, however, the major thrust of effort is now directed to the development of inorganic ion exchangers including zeolites such as mordenite, salts of a heteropoly acid such as ammonium

molybdophosphate, acidic salts of a polyvalent metal such as titanium phosphate and several insoluble ferrocyanides.

Each of these inorganic ion exchangers heretofore proposed has its own advantages and disadvantages so that none of them is quite satisfactory as a sorbent to be used in a high-level radioactive waste solution. For example, the zeolite-based sorbents are readily dissolved in an acidic solution so that they cannot be used in a highly acidic radioactive waste solution such as those coming from the purex process. The heteropolyacid salts and the acidic salts of a polyvalent metal are excellent in resistance against acid, although those of the latter class are not without problems in respect of adsorptive power and selectivity of adsorption in a highly acidic medium, but their high acid resistance alone is not sufficient to ensure their practical applicability, as is discussed in IAEA-TECDOC-337, page 31 (1985), another important characteristic in the sorbent is that sorption of the species of actinide elements is as small as possible. In this regard, ammonium molybdophosphate and titanium phosphate mentioned above are poor in selectivity for the separation of cesium and the actinide elements.

On the other hand, it is reported in AERE-R 11088, page 118 (1984) that most of the insoluble ferrocyanides have no sorptivity for the actinide elements. However, it is also reported, for example, in Journal of Nuclear Science and Technology, volume 4, page 190 (1987), Journal of Inorganic and Nuclear Chemistry, volume 34, page 1427 (1972) and elsewhere,that the sorptivity of an insoluble ferro-cyanide for cesium is subject to great variation depending on the medium which is acidic either with hydrochloric acid or with nitric acid, especially, when the concentration of the respective acid is high. Specifically, the sorptivity of insoluble ferrocyanides for cesium is greatly decreased in an aqueous solution of high nitric acid concentration. The presumable reason for this variation as discussed is the oxidation of the ferrocyanide into the corresponding ferricyanide in the strong nitric acid medium. This problem is particularly prominent in the copper-containing ferrocyanides which exhibit only very low sorptivity of cesium in an acidic aqueous solution of high nitric acid concentration. This fact is the basis of the well known technology that an aqueous solution of nitric acid of high concentration can be used as an excellent eluent for desorption of cesium sorbed on a copper-containing insoluble ferrocyanide as the sorbent. On the other hand, ammonium molybdophosphate as a typical sorbent for cesium is, as though having a high sorptivity for cesium, defective from the practical standpoint of the absence of an appropriate eluent for the desoprtion of the cesium sorbed on the sorbent.

In view of the above explained situation, it might be expected that an insoluble ferrocyanide compound could be a sorbent for cesium with greatly increased utilizability from an aqueous solution containing nitric acid in high concentration if oxidation of the ferrocyanide by the nitric acid could be effectively prevented. Unfortunately, it is usual that a highly reducing compound which might be a potential oxidation-preventing agent for ferrocyanides is readily oxidized by nitric acid, resulting in the loss of the oxidation-preventing power for ferrocyanides. Thus, it is eagerly desired to discover a compound having a high oxidation-preventing power for ferrocyanides even in very small amount but still insusceptible to oxidation by high-concentration nitric acid.

The present invention has an object to provide a novel method for removing cesium from an aqueous solution even when the solution contains nitric acid in a high concentration of, for example, 1M or higher, by the method of sorption on an insoluble ferrocyanide compound.

The present invention provides an improvement, in a method for removing cesium from an aqueous solution containing nitric acid by bringing the said aqueous solution into contact with an insoluble ferrocyanide compound as a sorbent to effect sorption of the cesium thereon, which comprises:
admixing the aqueous solution with an oxidation-preventing agent selected from hydrazinium compounds, i.e. hydrazine and salts thereof, amidosulphonic acid compounds including salts of an imido(bis)sulphuric acid or a nitrido(tris)sulphuric acid which can be hydrolyzed to form amidosulphonic acid in a strongly acidic medium, hydrogen peroxide, resorcine, hydroquinone, urea, thioglycolic acid and salts thereof, hydroiodic acid and salts thereof, sulfanilic acid and salts thereof, sulfanilamide, dihydroxytoluene, sulfanilhydrazine-p-sulphonic acid and salts thereof, and hydrazine compounds, e.g., methylhydrazine, phenylhydrazine, 1,1-diphenylhydrazine and tolylhydrazine, and salts thereof.

The insoluble ferrocyanide compound used in the present invention includes those compounds insoluble or scarcely soluble in water obtained by the precipitation reaction of a water-soluble ferrocyanide or ferrocyanic acid with a salt or hydroxide of a polyvalent metal other than alkaline earth elements. Such an insoluble ferrocyanide compound is exemplified typically by: potassium copper ferrocyanides $K_2Cu_3[Fe(CN)_6]_2$, $K_2Cu_5[Fe(CN)_6]_2$ and $K_2Cu_{11}[Fe(CN)_6]_2$, referred to as K_2Cu_3FC, K_2Cu_5FC and $K_2Cu_{11}FC$, respectively, hereinbelow; copper ferrocyanide $Cu_2Fe(CN)_6$, referred to as CuFC hereinbelow; potassium zinc ferrocyanide $K_2Zn_3[Fe(CN)_6]_2$, referred to as K_2Zn_3FC hereinbelow; zinc ferrocyanide $Zn_2Fe(CN)_6$, referred to as ZnFC hereinbelow; cadmium ferrocyanide $Cd_2Fe(CN)_6$, referred to as CdFC hereinbelow; nickel ferrocyanide $Ni_2Fe(CN)_6$, referred to as NiFC hereinbelow and cobalt ferrocyanide $Co_2Fe(CN)_6$, referred to as CoFC hereinbelow, though not specifically limited thereto. The sorbent used in the present invention is not limited to the

precipitates of these ferrocyanides per se but any solid material, such as silica gel and anion- and cation-exchange resins, supporting the ferrocyanide precipitated in its pores by in situ reaction can be used as well.

The improvement according to the present invention is applicable to cesium-containing aqueous solutions of which the concentration of nitric acid is 1M or higher or sufficient to cause oxidation of the ferrocyanide into ferricyanide but the invention is applicable to an aqueous solution of a lower nitric acid concentration. Specifically, the oxidation reaction of a ferrocyanide into ferricyanide proceeds at a substantial velocity even at room temperature when the concentration of nitric acid is 1M or higher although the exact velocity of the oxidation reaction depends on various factors such as the kind of ferrocyanide, treatment temperature and other factors. The oxidation reaction of the ferrocyanide into ferricyanide can be almost completely prevented according to the present invention even when the concentration of nitric acid in the aqueous solution is 3M or higher so that the sorptive capacity of the ferrocyanide for cesium can be as large as that in the absence of nitric acid in the solution.

The characteristic feature of the inventive improvement consists in the admixture of a specific oxidation-preventing agent listed above to the cesium-containing aqueous solution of high nitric acid concentration. It should be noted that a compound having a high reducing power for a ferricyanide compound into ferrocyanide is not always suitable as the oxidation-preventing agent for the ferrocyanides. Among the above listed oxidation-preventing agents, for example, urea, resorcine and amidosulphonic acid have no reducing power for ferricyanides as compared with conventional strong reducing agents such as hydroxylammonium salts, sulphites, thiosulphates and dithionites. Nevertheless, the effectiveness of hydroxylammonium salts, sulphites, thiosulphates and dithionites as an oxidation-preventing agent for ferrocyanides is much lower than that of urea, resorcine and amidosulphonic acid according to the results of the experiments undertaken by the Applicants. Whereas hydrogen peroxide is known to act as an oxidizing agent for ferrocyanide ions under an acidic conditions, hydrogen peroxide exhibits an oxidation-preventing effect for ferrocyanides in a strongly acidic medium. In contradiction to the generally accepted understanding that a compound having a higher reducing power would be more readily oxidized by nitric acid when the concentration of nitric acid is high, it has been quite unexpectedly discovered that the above mentioned specific oxidation-preventing agents are immune to oxidation by nitric acid but retain oxidation-preventing power for ferrocyanides even when their concentration is very low. Thus, the listing given above of oxidation-preventing agents for ferrocyanides is not a result of the selection of reducing power for ferricyanides but is an unexpected result obtained only after elaborate experimentation undertaken by the Applicants. The above described findings are suggestive of the mechanism of the effective oxidation prevention by the above proposed oxidation-preventing agents which is not in direct correlation with the reducing power of the compounds. In particular, hydrazinium compounds, such as hydrazine and salts thereof, and amidosulphonic acid compounds, such as amidosulphonic acid and salts thereof, are preferable due to their outstandingly high oxidation-preventing activity, exhibiting the desired effect even when their concentration in aqueous solution is very low, in the range, for example, from 5×10^{-6} to 1×10^{-4} M in the sorption of cesium on a potassium copper ferrocyanide from an aqueous solution containing nitric acid in a concentration of 3M.

The effectiveness of the oxidation-preventing agents listed above depends on the kind of insoluble ferrocyanide compound used as the sorbent. This is presumably dependent on the sorptive power of the corresponding ferricyanide compound for cesium. The insoluble ferrocyanide compounds in general have a higher sorptive power for cesium than the corresponding ferricyanide compounds so that the improvement of the invention can be obtained more or less in any of the insoluble ferrocyanide compounds. For example, the effectiveness of the inventive improvement is very pronounced for copper-containing ferrocyanide compounds as the sorbent as a consequence of the very low sorptive power of the corresponding copper-containing ferricyanide compounds for cesium. Therefore, recovery of cesium sorbed on copper-containing insoluble ferrocyanide can be efficiently performed by using an aqueous nitric acid solution of high concentration containing no oxidation-preventing agent as the eluent.

In the following, the improvement provided by the present invention is described in more detail by way of examples and comparative examples, which, however, do not limit the scope of the invention in any way since the optimum conditions for the actual removal of cesium from an aqueous solution naturally depend on various factors including the composition of the aqeuous solution from which cesium is to be removed.

In the following examples, the effectiveness of the respective oxidation-preventing agents was evaluated in terms of the distribution coefficient Kd given by the equation:

$$Kd, ml/g = (C_0 - C)/C \times L/W,$$

in which C_0 is the concentration of cesium in the starting aqueous solution, C is the concentration of cesium in the aqueous solution after removal by sorption, L is the volume of the aqueous solution in ml, and W is the amount of the sorbent in g. Determination of the concentration of cesium in the aqueous solution was performed for the solution with admixture of potassium chloride in a concentration of 0.1M as a sensitizer by the method

of atomic absorption spectrophotometry or atomic emission spectrometry each using an air-acetylene flame.

Example 1.

Several insoluble ferrocyanide compounds were prepared to serve as a sorbent for cesium including: ZnFC, CdFC, two kinds of CuFC, i.e. CuFC-A and CuFC-B, NiFC and CoFC obtained as precipitates by admixture of an aqueous solution of sodium ferrocyanide with an aqueous solution of zinc nitrate, cadmium chloride, copper (II) chloride, copper (II) sulfate, nickel (II) chloride and cobalt (II) nitrate, respectively, in an amount such that the molar ratio of the transition metal element to the ferrocyanide ions was at least 2 followed by separation of the precipitates by filtration, washing with water and air-drying as the insoluble ferrocyanides of simple-salt form; and K_2Zn_3FC, K_2Cu_3FC, K_2Cu_5FC and $K_2Cu_{11}FC$ obtained as precipitates by admixture of an aqueous solution of potassium ferrocyanide with an aqueous solution of zinc sulphate or copper (II) sulphate in a stoichiometric amount corresponding to the respective molar ratio of potassium to zinc or copper in the product precipitates followed by separation of the precipitates by filtration, washing with water and air-drying as the insoluble ferrocyanides of the double-salt form.

In addition, two more insoluble ferrocyanide compounds, i,e. potassium cobalt ferrocyanide and molybdic acid ferrocyanide, referred to as KCoFC and MoO_3FC, respectively, hereinbelow, were prepared. Thus, the KCoFC was prepared according to the teaching of Prout et al. in Journal of Inorganic and Nuclear Chemistry, volume 27, page 473 (1965) from potassium ferrocyanide and cobalt nitrate in a molar ratio of Co:Fe of 1.44 although no analytical data were available for the exact chemical composition of the KCoFC. The MoO_3FC was prepared according to the teaching of Baestle et al. in Journal of Inorganic and Nuclear Chemistry, volume 26, page 1329 (1964) and volume 27, page 683 (1965) from sodium molybdate, sodium ferrocyanide and hydrochloric acid in a molar ratios of Mo:Fe of 2.40 and H^+:Mo of 2.67 although no analytical data were available for the exact chemical composition of the MoO_3FC.

Each of the insoluble ferrocyanide compounds prepared above was taken in an exact amount of 0.01 g calculated as anhydrous compound in a stoppered Erlenmeyer flask to which 10 ml of an aqueous solution, of which the concentration of nitric acid was 3M, containing cesium chloride in a concentration of 1×10^{-3}M and hydrazine sulphate in a concentration of 2×10^{-4}M. The flask was stoppered and shaken for 7 days in a water bath thermostatted at 25 °C. After subjecting the solution to solid-liquid separation by filtration, a portion of the filtrate was taken and analyzed for the concentration of cesium therein and the value of Kd was calculated to give the results shown in Table 1 below. Comparison of these results with those in Comparative Example 1 and Reference Example 1 described below led to the conclusion that the value of Kd in the nitric acid solution could be as high as in a hydrochloric acid solution of the same molar concentration when the aqueous solution contained a small amount of the hydrazine compound.

Comparative Example 1.

The experimental procedure was just the same as in Example 1 described above except for omission of the hydrazine sulphate added to the aqueous solution as the oxidation-preventing agent. The values of Kd obtained as a result are shown also in Table 1.

Reference Example 1.

The experimental procedure was just the same as in Example 1 described above except for replacement of nitric acid with the same molar amount of hydrochloric acid and omission of the hydrazine sulphate added to the aqueous solution as the oxidation-preventing agent. The values of Kd obtained as a result are shown also in Table 1.

Table 1

Sorbent	Kd, ml/g		
	Example 1	Comparative Example 1	Reference Example 1
K_2Cu_3FC	3.0×10^5	2.3×10^2	3.4×10^5
K_2Cu_5FC	2.2×10^5	1.1×10^2	3.3×10^5
$K_2Cu_{11}FC$	2.7×10^4	7.8×10^1	7.3×10^4
CuFC-A	1.0×10^4	1.1×10^2	4.4×10^4
CuFC-B	4.3×10^3	9.2×10^1	2.7×10^4
K_2Zn_3FC	1.1×10^3	4.5×10^1	2.1×10^3
ZnFC	1.1×10^3	4.9×10^1	3.6×10^3
CdFC	3.8×10^5	5.6×10^3	8.2×10^4
NiFC	4.1×10^4	3.7×10^2	2×10^7
CoFC	at least 10^8	4.3×10^3	2×10^7
KCoFC	7.9×10^2	1.0×10^2	1.4×10^3
MoO_3FC	1.1×10^2	3.1×10^1	1.4×10^3

Example 2.

The experimental procedure using K_2Cu_3FC as the sorbent was substantially the same as in Example 1 except that the concentration of hydrazine sulphate was 5×10^{-6}M instead of 2×10^{-4}M and shaking of the flask was terminated after 1 hour. The value of Kd was 2.0×10^4 ml/g as calculated from the residual concentration of cesium of 4.70×10^{-5}M in the filtrate obtained by filtration.

Comparative Example 2.

The experimental procedure using K_2Cu_3FC as the sorbent was substantially the same as in Example 2 except for omission of the hydrazine sulphate added to the aqueous solution as the oxidation-preventing agent. The value of Kd was 5.0×10^2 ml/g as calculated from the residual concentration of cesium of 6.67×10^{-4}M in the filtrate obtained by filtration.

Example 3.

Several experiments were undertaken using K_2Cu_3FC each under substantially the same conditions as in Example 2 except that the concentration of hydrazine sulphate as the oxidation-preventing agent was varied and shaking of the flask was continued for 24 hours. The values of Kd obtained in these experiments are shown

by the curve (a) in Figure 1. As is clear from this graph, a critical value was found in the concentration of hydrazine sulphate at about 5 x 10^{-6}M at which the value of Kd showed a rapid increase as the concentration of hydrazine sulphate was increased.

Comparative Example 3.

The experimental procedure was substantially the same as in Example 3 except for omission of hydrazine sulphate. The value of Kd was 2.9 x 10^{2} ml/g as calculated from the residual concentration of cesium of 7.76 x 10^{-4}M in the filtrate obtained by filtration.

Example 4.

The experimental procedure with varied concentrations of hydrazine sulphate was substantially the same as in Example 3 except that the concentration of nitric acid was 6M instead of 3M. The values of Kd obtained in these experiments are shown by the curve (b) in Figure 1. As is clear from this graph, the value of Kd began to increase rapidly at about 3 x 10^{-3}M of hydrazine sulphate concentration as its concentration was increased although this concentration was less critical than in the curve (a).

Comparative Example 4.

The experimental procedure was substantially the same as in Example 4 except for omission of hydrazine sulphate. The value of Kd was 9.6 x 10^{1} ml/g as calculated from the residual concentration of cesium of 9.12 x 10^{-4}M in the filtrate obtained by filtration.

Example 5.

Several experiments were undertaken using K_2Cu_3FC as the sorbent under substantially the same conditions as in Example 3 except that, in place of the hydrazine sulphate as the oxidation-preventing agent, amidosulphonic acid was added to the aqueous solutions in varied concentrations. The values of Kd obtained in these experiments are shown in Figure 2 as a function of the concentration of amidosulphonic acid. As is clear from this graph, a critical concentration of the oxidation-preventing agent was found at about 10^{-4}M.

Example 6.

The experimental procedure using K_2Cu_3FC was substantially the same as in Example 2 except that the hydrazine sulphate as the oxidation-preventing agent was replaced with one of the compounds listed in Table 2 each in the concentration indicated in the same table and shaking of the flask was continued for 24 hours. The values of Kd as calculated from the respective residual concentrations of cesium in the filtrates obtained by filtration are also shown in the table.

Comparative Example 5.

The experimental procedure using K_2Cu_3FC was substantially the same as in Example 6 except that the oxidation-preventing agent was replaced by hydroxylamine hydrochloride, sodium thiosulphate, sodium sulphite or sodium dithionite each in a concentration indicated in Table 2 or entirely omitted. The values of Kd as calculated from the respective residual concentrations of cesium in the supernatant are also shown in the table.

Table 2

	Oxidation-preventing agent		Concentration of remaining cesium, M	Kd, ml/g
	Kind	Concentration, M		
Example 6	Hydrogen peroxide	2×10^{-3}	4.07×10^{-5}	2.4×10^{4}
	Resorcine	5×10^{-4}	3.62×10^{-6}	2.8×10^{5}
	Hydroquinone	1×10^{-3}	3.77×10^{-6}	2.6×10^{5}
	Urea	7×10^{-3}	5.14×10^{-5}	1.8×10^{4}
	Sodium thioglycolate	1×10^{-5}	3.07×10^{-6}	3.2×10^{5}
	Potassium iodide	5×10^{-4}	3.42×10^{-6}	2.9×10^{5}
	Sulfanilic acid	1×10^{-3}	3.47×10^{-6}	2.9×10^{5}
	Sulfanilamide	1×10^{-3}	3.40×10^{-6}	2.9×10^{5}
	2,5-Dihydroxytoluene	8×10^{-5}	3.15×10^{-6}	3.2×10^{5}
	3,4-Dihydroxytoluene	1×10^{-4}	3.19×10^{-6}	3.1×10^{5}
	2,4-Dihydroxytoluene	1×10^{-3}	3.19×10^{-6}	3.1×10^{5}
	3,5-Dihydroxytoluene	1×10^{-3}	3.41×10^{-6}	2.9×10^{5}
	Methylhydrazine sulphate	1×10^{-4}	3.40×10^{-6}	2.9×10^{5}
	Phenylhydrazine hydrochloride	1×10^{-4}	3.26×10^{-6}	3.1×10^{5}
	Sulfanilhydrazine-p-sulphonic acid	1×10^{-4}	2.54×10^{-6}	3.9×10^{5}
	1,1-Diphenylhydrazine hydrochloride	1×10^{-4}	3.10×10^{-6}	3.2×10^{5}
	o-Tolylhydrazine hydrochloride	1×10^{-3}	3.03×10^{-6}	3.3×10^{5}
	p-Tolylhydrazine hydrochloride	1×10^{-3}	3.29×10^{-6}	3.0×10^{5}
Comparative Example 5	Hydroxylamine hydrochloride	1×10^{-2}	7.93×10^{-4}	2.6×10^{2}
	Sodium thiosulphate	1×10^{-2}	6.25×10^{-4}	6.0×10^{2}
	Sodium sulphite	1×10^{-2}	7.11×10^{-4}	4.1×10^{2}
	Sodium dithionite	1×10^{-2}	6.36×10^{-4}	5.7×10^{2}
	None	-	7.76×10^{-4}	2.9×10^{2}

Claims

1. A method for removing cesium from an aqueous solution containing nitric acid which process comprises bringing the said aqueous solution into contact with an insoluble ferrocyanide compound as a sorbent to effect sorption of the cesium thereon, wherein the improvement comprises admixing the aqueous solution with an oxidation-preventing agent selected from hydrazinium compounds, amidosulphonic acid compounds, hydrogen peroxide, resorcine, hydroquinone, urea, thioglycolic acid and salts thereof, hydroiodic acid and salts thereof, sulfanilic acid and salts thereof, sulfanilamide, dihydroxytoluene, sulfanilhydrazine-p-sulphonic acid and salts thereof, methylhydrazine and salts thereof, phenylhydrazine and salts thereof, 1,1-diphenylhydrazine and salts thereof and tolylhydrazine and salts thereof.

2. A method as claimed in claim 1 in which the oxidation-preventing agent is a hydrazinium compound or an amidosulphonic acid compound.

3. A method as claimed in claim 1 or claim 2 in which the concentration of the oxidation-preventing agent in the aqueous solution is from 5×10^{-6}M to 1×10^{-4}M.

4. Use of the method as claimed in any one of claims 1 to 3 in the reprocessing of spent nuclear fuels.

FIG. 1

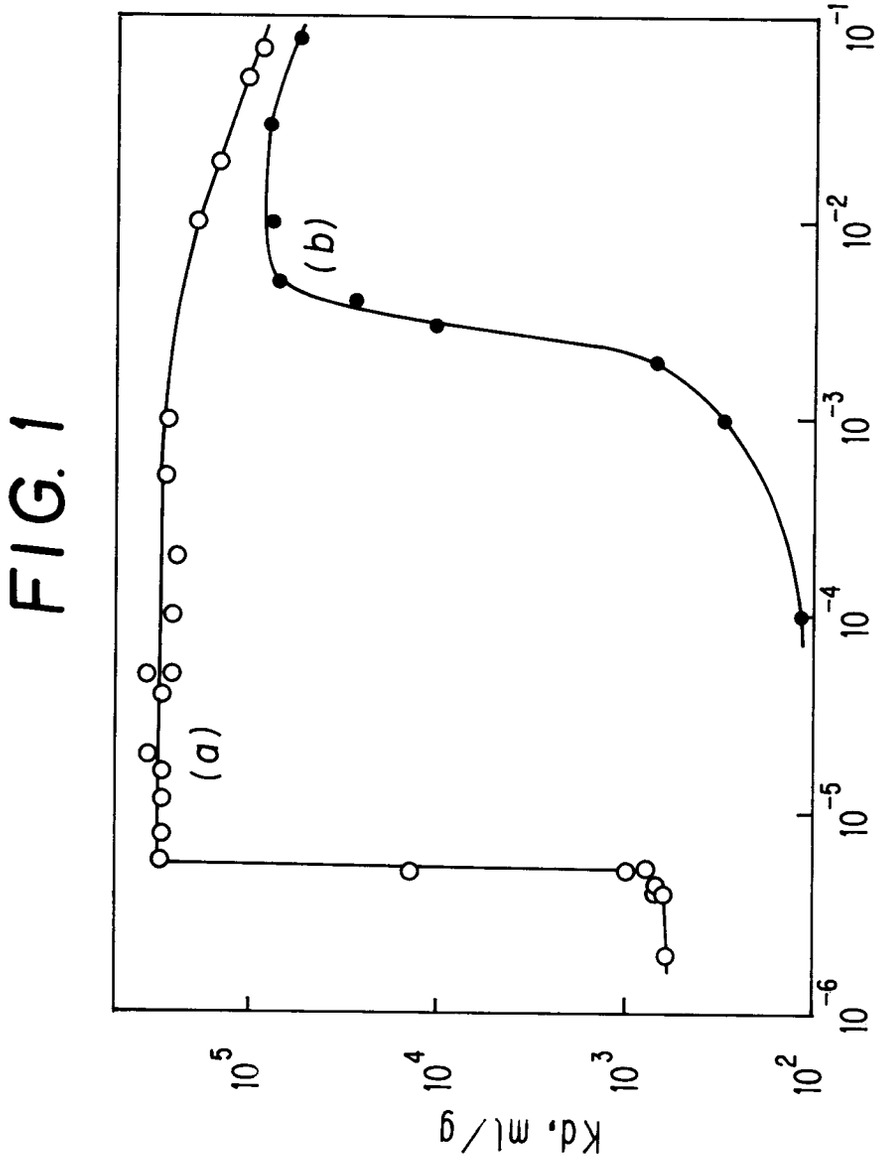
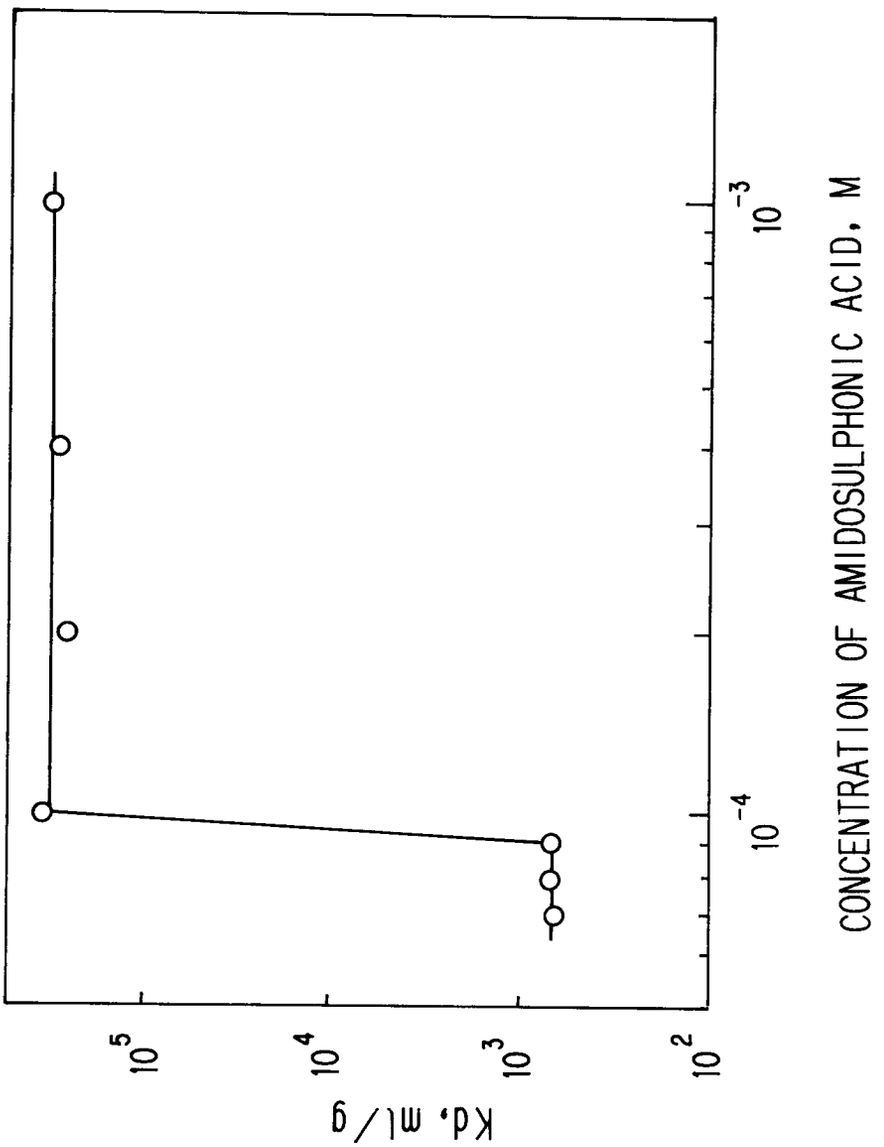

Kd, ml/g
10^5
10^4
10^3
10^2
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
(a)
(b)
CONCENTRATION OF HYDRAZINE SULPHATE, M

FIG. 2


Kd, ml/g
10^5
10^4
10^3
10^2
10^{-4}
10^{-3}
CONCENTRATION OF AMIDOSULPHONIC ACID, M

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 7879

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	US-A-3 296 123 (PROUT) 3 January 1967 * claims 1,4; example 1 *	1,2,4	G21F9/12
Y	FR-A-2 548 042 (SUMIMOTO) 4 January 1985 * page 3, line 21 - page 4, line 2; claim 1 *	1,2,4	
A	FR-A-2 346 817 (C.E.A) 28 October 1977 * claims 1,3 *	1-4	
A	US-A-3 896 045 (PEETERS) 22 July 1975 * abstract; claims 1,5; table 3 *	1-4	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G21F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 DECEMBER 1991	NICOLAS H.J.F.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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