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(54) **Waste treatment**

(57) In the treatment of wastes, such as liquid radioactive effluents, it is known to remove radionuclides by successive *in situ* precipitation of cobalt sulphide, an hydroxide, barium sulphate and a transition element ferrocyanide, followed by separation of the thereby decontaminated effluent.

In this invention, use is made of precipitates such as obtained above in the treatment of further fresh liquid radioactive effluent, when it is found that the precipitates have additional capacity for extracting radionuclides. The resulting supernatant liquor may then be subjected to a further precipitation treatment such as above. Decontamination factors for radionuclides of Ce, Ru, Sr and Cs have been considerably enhanced.

GB 2 073 477 A

## SPECIFICATION

## Waste treatment

- 5 This invention relates to the decontamination of liquid radioactive effluents. 5
- Radio-nuclides present in liquid radioactive effluents such as effluents arising from the reprocessing of irradiated nuclear fuel have been precipitated for two purposes, firstly to reduce the radioactivity in the effluent to a level at which it may be discharged, for example into the sea, and secondly to concentrate the radio-nuclides into as small a volume as possible for storage purposes. British Patent Specification No
- 10 1,211,816 describes a method of decontaminating liquid radioactive effluents by, after optional oxidation of the effluent, forming successively *in situ* and without separation of the respective precipitates, precipitates of ferrous sulphide and hydroxide, barium sulphate and a ferrocyanide of a transition element, the pH being between 7 and 9 at the end of the treatment, and the combined precipitates then separated from the decontaminated effluent. Part of the radio-nuclide content of the effluent thereby becomes incorporated into
- 15 the precipitates by processes such as adsorption on the surface of the precipitates, co-precipitation by isomorphism and ion-exchange on the precipitates. 15
- When the above process is used to treat an effluent comprising a solution produced by dissolution of irradiated Mg/Zr alloy clad fuel elements in nitric acid, it is generally found that decontamination factors of about 150 may be achieved for  $\beta$ -emitting radionuclides and that decontamination factors of  $>1000$  may be
- 20 achieved for  $\alpha$ -emitting radionuclides. However, in order to discharge treated effluent into the sea, decontamination factors of the order of 1000 are currently required. 20
- It has now been surprisingly found according to the present invention that precipitates obtained in decontamination processes such as described before have additional capacity for incorporating radio-nuclides therein and that use may be made of this capacity in the decontamination of further liquid
- 25 radioactive effluent in order to meet the aforementioned requirements. 25
- Thus, the present invention provides a method of decontaminating liquid radioactive effluents comprising
- (i) forming precipitates in the effluent to extract radionuclides from the effluent into the precipitates;
- (ii) separating the combined precipitates from the effluent;
- 30 (iii) contacting the separated combined precipitates with fresh liquid radioactive effluent thereby to extract radionuclides from the fresh effluent into the combined precipitates; and 30
- (iv) removing the supernatant effluent resulting from step (iii) and forming precipitates therein to extract radionuclides from the effluent into the precipitates.
- 35 The precipitates may then be separated to give a decontaminated effluent. 35
- In certain test experiments, Decontamination Factors of radionuclides of Cs, Sr and Ce were improved by a factor of 2-30 by the above method in comparison with the prior art method. The invention therefore gives rise to a treated effluent which is more suitable for safe discharge than hitherto. Also, the invention makes more effective use of the capacity of the precipitates to contain radio-nuclides and is therefore capable of
- 40 giving rise to a reduced volume of precipitates, for example half that obtained hitherto. This is a desirable aim since, ultimately, such precipitates have to be treated and stored in a safe environment. 40
- An example of a liquid radioactive effluent to which the present invention may be applied is the effluent arising as a result of the handling of irradiated fuel from the first generation of British nuclear power stations. Thus, irradiated uranium metal fuel encapsulated in a magnesium (Mgnox) alloy is decanned and the
- 45 separated Mgnox cladding dissolved in nitric acid; solids are removed and a large proportion of the U and Pu content of the resulting solution is extracted by solvent extraction in accordance with methods known in the art. The remaining aqueous solution constitutes a liquid radioactive effluent and may include for example, ions of Mg, Al, Fe, Ca, U, Pu, Sb, Ce, Sr, Cs and Ru wherein the radionuclides  $Ce^{144}$ ,  $Sr^{90}$ ,  $Cs^{137}$  and  $Ru^{106}$  are particularly noteworthy as radioactive contaminants. 45
- 50 The Mg and Al arise from the canning material. The Fe and Ca arise from incidental additions during storage and the U and Pu are constituted by residual fuel which adhered to the Mgnox cladding during the mechanical decanning process and which was incompletely extracted during the above mentioned solvent extraction process. The Sb, Ce, Sr, Cs and Ru arise as fission products of the original irradiation process. 50
- The precipitates produced in step (i) and step (iv) may be precipitates known in the art for removing
- 55 radioactive nuclides from liquid radioactive effluents and, as is known in the art, their order of production and the conditions under which they are produced (such as pH) may be selected to optimise the removal of particular radionuclides from the effluent. The selection of precipitates and their conditions of production will be determined by the composition of the liquid radioactive effluent. Where the effluent arises from the first generation of British nuclear power stations and has a constitution as indicated above, sulphate ions
- 60 may be added initially so that  $BaSO_4$  may subsequently be precipitated. A transition metal (eg Ni) ferrocyanide may then be precipitated; this removes Cs, probably by an ion exchange mechanism. Sulphide ions may next be provided and  $Ba^{++}$  ion added to precipitate  $BaSO_4$  and remove SR by isomorphous precipitation of  $SrSO_4$ .  $Co^{++}$  ions may be added to precipitate  $CoS$  which removes Ru by ion exchange.  $Al(OH)_3$  will be precipitated at some stage during addition of OH ions and it is believed that this probably
- 65 removes Ce, possibly by a co-precipitation or by adsorption onto the  $Al(OH)_3$ . 65

It has been found that increasing the pH to about 6.5 during step (iii) increases the decontamination factors of Ce, Sr, Cs and Ru.

The invention will now be particularly described by way of example only as follows:

- 5 **Example** 5
- A volume (100 to 200 ml) of simulated liquid radioactive effluent solution in 0.5M HNO<sub>3</sub> and of the following composition was prepared:-
- |    |    |          |              |    |
|----|----|----------|--------------|----|
| 10 | Mg | 20 g/l   | Cs 1.16 mg/l | 10 |
|    | Al | 0.14 g/l | Sr 0.35 mg/l |    |
|    | Fe | 0.35 g/l | Ru 0.95 mg/l |    |
| 15 | Ca | 0.5 g/l  | Ce 0.97 mg/l | 15 |
- The listed elements were, of course, present in ionic form. Small quantities of the radioactive nuclides Cs<sup>137</sup>, Sr<sup>85</sup>, Ru<sup>103</sup> and Ce<sup>144</sup> were added in the form of their chlorides, ie the solution was 'spiked'.
- 20 **Step (i)** 20
- The simulated solution was then treated by the following additions in sequence: -SO<sub>4</sub><sup>=</sup>, OH<sup>-</sup>, Ni<sup>2+</sup> and Fe(CN)<sub>6</sub><sup>4-</sup>, OH<sup>-</sup>, S<sup>=</sup>, Ba<sup>2+</sup>, Co<sup>2+</sup>, OH<sup>-</sup>, flocculating aid. This gave precipitates including Ni<sub>2</sub>Fe(CN)<sub>6</sub>, BaSO<sub>4</sub> and CoS.
- 25 After 1½ hours settling, the decontamination factors in respect of Ce, Ru, Sr and Cs were determined by standard methods and then additional Ba<sup>2+</sup> together with a flocculating aid added to precipitate further BaSO<sub>4</sub>. After 1½ hours settling, the decontamination factors were again determined. 25
- Step (ii)**
- The supernatant liquor was drawn off to separate the precipitates.
- 30 **Step (iii)** 30
- The precipitates were stirred for 1 hour with a similar volume of fresh simulated liquid radioactive effluent, the pH having been adjusted to 6.5 to precipitate hydroxides of Al and Fe. After 2 hours settling, the decontamination factors were again determined.
- 35 **Step (iv)** 35
- The supernatant liquor from step (iii) was drawn off, re-spiked and subjected to the same treatment as described above in step (i),
- A final measurement of decontamination factors was carried out after a still further settling of 2 hours.
- 40 The decontamination factor (or D F) values obtained are summarised in the table below in respect of two separate experiments, designated experiments 1 and 2 respectively. A decontamination factor in respect of a particular nuclide is the ratio of its total activity present before and after a particular treatment. It should be noted that, in view of the low concentration of the radionuclides in solution, the statistical accuracy of the decontamination factors is not high and that there is necessarily some scatter of results from one experiment
- 45 to another. The steps referred to in the table correspond to those in the above description, and the measurements were taken at the stages described above. 45

## Radionuclide and Experiment Number

5	Step	Ce		Ru		Sr		Cs		5
		1	2	1	2	1	2	1	2	
10	(i)									
	before Ba <sup>2+</sup> addition	263	383	1600	1145	44	52	740	926	10
	after Ba <sup>2+</sup> addition	1380	1400	1910	859	1560	1390	2130	1900	
	(iii)	102	103	491	554	28	25	487	584	
15										15
	(iv)									
	before Ba <sup>2+</sup> addition	66	101	115	97	87	53	227	245	
	after Ba <sup>2+</sup> addition	322	277	124	85	326	245	157	123	
20	final measurement	372	319	124	91	304	318	167	140	20
	Overall D F									
	Product of steps	~35,000		~50,000		~8,000		~75,000		
	(iii) and (iv)									
25										25
	Additional experiments have been carried out which show that in a process according to the present invention, considerable economies can be made in the use of precipitating reagents, whilst still producing a final effluent with decontamination factors within permissible limits for discharge of the effluent into the sea.									
30	CLAIMS									30
	1. A method of decontaminating liquid radioactive effluents comprising the steps of									
35	(i)	forming precipitates in the effluent to extract radionuclides from the effluent into the precipitates;								35
	(ii)	separating the combined precipitates from the effluent;								
	(iii)	contacting the separated combined precipitates with fresh liquid radioactive effluent thereby to extract radionuclides from the fresh effluent into the combined precipitates; and								
40	(iv)	removing the supernatant effluent resulting from step (iii) and forming precipitates therein to extract radionuclides from the effluent into the precipitates.								40
	2. A method according to claim 1 further comprising separating decontaminated effluent from the precipitates formed in step (iv).									
	3. A method according to claim 1 or 2 comprising adding sulphate ions, sulphide ions, cobalt ions, hydroxide ions and ferrocyanide ions to the effluent in steps (i) and (iv).									
45	4. A method according to claim 1, 2 or 3 comprising adjusting pH to about 6.5 during step (iii).									
	5. A method of decontaminating liquid radioactive effluents according to claim 1 and substantially as herein described.									