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(54) METHOD FOR LIQUID RADIOACTIVE WASTE REPROCESSING (AND VARIANTS)

(57) The inventive methods are used for liquid radioactive waste (LRW) reprocessing by immobilizing radionuclides into a crystal material. Said methods consist in the synthesizing of insoluble compounds which immobilise long-livid radionuclides. The insoluble compounds in the form of salts or oxides arc synthesised in hydrothermal conditions in a flow by passing LRWs being processed and reagents required for the synthesis through a layer of the insoluble particles at a speed enabling synthesizable radionuclide-containing compounds to be crystallized on the surface of the particles of the layer. Said insoluble particles are embodied in the form of metal oxides, for example, iron, manganese, cobalt, zirconium oxides or salts, for example, hydroxylapatite. The hydrothermal synthesis is carried out at a temperature range from 180°C to 250°C and a pressure range from 20 to 150 atm.

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Description

Technical Field

[0001] The invention relates to protection of the environment, namely methods for liquid radioactive waste (LRW) reprocessing comprising immobilizing same into a crystal material, acceptable from the viewpoint of ecology and the invention can be used at facilities of atomic power industry and chemical-metalurgical production lines.

Background Art

[0002] Liquid radioactive waste reprocessing is connected with the necessity to attain a safe long-term storage of radioactive waste (RAW), for which purpose hard radioactive waste (HRW) change into a state providing for a minimum leaching-out of radionuclides with natural waters. This task is solved by conventional methods such as bituminization, cementation and vitrification of RAW (patent RU N 2088986, 27.08.1997; patent RU N 2271586, 10,03.2006; patent RU N 2131152, 27,05.1999; Donald I.W., Metcalfe B.L., Taylor R.N.J. the immobilization of high level radioactive wastes using ceramics and glasses. Review. Journal of Materials Science, 32, 1997. p. 5856-5862), The least degree of leaching is provided with RAW vitrification and has a value of about 10^{-6} g/cm. day.

[0003] By now a marked interest is shown in oxide materials as matrices for the concentration and solidification of solutions of radionuclides salts and heavy metals usable in processes for treatment of liquid radioactive wastes- Such a form of burial of waste material is most promising as affording higher radioactive, chemical and thermal stability as against the methods as mentioned hereinabove.

[0004] Such forms of RAW immobilization are ceramic material widely known by the trade name Syncron whose matrix is normally a combination of hollandite ($BaAl_2Ti_2O_6$ or $BaAl_2Ti_6O_{16}$), perovskite ($CaTiO_3$) and zirconolite ($CaZrTi2O_7$).

[0005] A great number of works are dedicated to the synthesis and use of ceramics Synroc for immobilizing RAW patent RU N 2153717, 27.07.2000, EP N 0007236, 23.01.1980; US N 4274976, 23.06.1981; Ringwood A.E., Kesson S.E., Reeve K.D., Levins D.M., Ramm E.J. Synroc. In: Radioactive Waste Forms for the Future Eds. Lutze W, and Ewing R.C. Amsterdam: Elsevier Science Publishers B.V., 1988. P. 233-334; Donald I.W., Metcalfe B.L., Taylor R.N.J. The immobilisation of high level radioactive wastes, using ceramic and glasses. Review. Journal of Materials Science, 32, 1997, p. 5862-5865 et al.). Materials of this type allow to reduce the degree of RAW leaching from a ceramic matrix up to 10^{-9} g/cm^2 .day.

[0006] Said methods of RAW reprocessing in which radio active wastes are immobilized into a ceramic matrix have, alongside the aforesaid advantages, some defects, which arc attributable to the high power capacity of high-temperature processes carried out at 1000°C or higher, a multitude operations and the necessity to employ special equipment.

[0007] Besides, it should be noted that the use of ceramic Synroc is effective in the case of small RAW volumes being immobilized, highly active wastes (HAW) for the most part.

[0008] In recent years much work has been done on the hydrothermal synthesis of ceramic materials and minerals suitable for immobilizing radionuclides in RAW reprocessing.

[0009] A rale of crystal growth through hydrothermal synthesis is increased many a time as against synthesis at normal temperatures, which hydrothermal synthesis presents new opportunities for selectively recovering radionuclides, However, the number of ceramic materials hydrothermally synthesized and capable of immobilizing the radionuclides is very limited. (Johnson CD., Skakle J.M. S., Johnson M.G, Feldmann J. Macphee D.E. Hydrothermal synthesis, crystal structure and acqueous stability of two cadmium arsenate phases, $CdNH4(HAsO4)OH$ and $Cd5H2(AsO4)4\text{-}4H2O$.J. Mater.Chem. 2003, 13,1429-1432).

[0010] Hydrothermal methods of reprocessing radioactive wastes go to show that the basic problems of LRW hydrothermal purification from radionuclides are as follows

- selection of a type of ceramic matrix produced due to hydrothermal synthesis, which should be selective toward the corresponding radionuclides-,
- ceramic matrix is formed in treatable LRW media (pH, composition of salt and other) while introducing suitable agents into solution at predetermined temperatures and pressure in a system;
- separation coefficient "ceramics-solution" should be great enough for a coefficient to be provided to purify the solution from the radionuclides.

[0011] Sorption reactant materials (SRM) are the new promising materials for the recovery of radionuclides.

[0012] The principle of operation of sorption-reactant materials resides in continuously forming an insoluble compound sorbing radionuclides in a porous matrix of inert material, with a continuous growth of crystals of the insoluble compound concurrently with sorption of the radionuclides. The result: there form crystal materials with a very small interface surface and sorbed radionuclides distribute over entire volume of the crystal material; such being the case, the leaching of radionuclides from sorption-reactant materials is by several orders lower than from selective ion- exchange sorbents having a large exchange capacity and, as so, a large interface surface.

[0013] Thus, patent RU N 2185671 20.07.2002 discloses the recovery of strontium radionuclides from solutions with a high content of hardness salts and liquid radioactive wastes of a complex chemical composition. SRMs are formed directly in the process of purification due to reaction of a starting sorption-reactant material comprising barium exchange cations, with a sulfate-ion purifying containing solution with the formation of insoluble barium sulfate crystallzable in the matrix of the sorption-reactant material.

[0014] This method is the closest prior art to the method sought for protection.

Disclosure of invention

[0015] An object of the present invention is to provide of a method of reprocessing liquid radioactive wastes containing long-lived radionuclides, preferably cobalt, manganese and strontium in hydrothermal conditions, which provides a high degree, of purification of solutions from radionuclides, as required, a high reparation coefficient (a ratio of purified LRW/HRW volumes), formation of a strong durable ceramic matrix with a minimum leaching-out of the radionuclides.

[0016] The problem is solved by a method of reprocessing liquid radioactive wastes containing long-lived radionuclides by synthesis of insoluble compounds immobilizing the long-lived radionuclides in hydrothermal conditions in a flow by passing LRW being treamed and reagents required for synthesis thought a layer of insoluble particles at a speed enabling synthesizable radionuclide-containing compounds to be crystallized on the surface of the particles of the layer.

[0017] The most favorable conditions for hydrothermal synthesis are temperature of 180-250°C and pressure of 20-150 atm.

[0018] Insoluble particles used arc preferably represented by metal oxides or salts thereof.

[0019] Metal oxides used arc represented by ferric oxide and/or manganese oxide and/or cobalt oxide and salts, by hydroxylapatite.

[0020] In a second alternative embodiment, the problem is solved by a method of reprocessing liquid radioactive wastes containing long-lived radionuclides by synthesis of insoluble compounds immobilizing long-lived radionuclides into a crystal lattice, with synthesis of a crystal phase in the form of oxides in hydrothermal conditions in a flow by passing LRWs being treated and reagents required for the synthesis through a layer of metal oxides at a speed enabling synthesizable radionuclide-containing oxides to be crystallized on the surface of the particles of the layer of oxides.

[0021] Preferably transition metal oxides used are represented by ferric oxide and/or manganese oxide and/or cobalt oxide and/or zirconium oxide.

[0022] It is most favorable to carry out the hydrothermal synthesis at a temperature range between 180 and 250°C and a pressure between 20 and 150°C.

[0023] The third alternative embodiment provides the method of reprocessing liquid radioactive wastes containing long-lived radionuclides by synthesis of Insoluble compounds immobilizing the long-lived radionuclides into a crystal lattice in hydrothermal condition, in a flow by passing LRWs being treated and reagent required for the synthesis through a layer of transition metal oxides at a speed enabling synthesizable radionuclide - containing compounds to be crystallized on the surface of the particles of the layer of oxides.

[0024] Preferably transition metal oxides used are represented by ferric oxide and/or manganese oxide and/or cobalt oxide and/or zirconium oxides.

[0025] It is most favourable to carry out hydrothermal synthesis at a temperature comprised between 180 and 250°C and a pressure between 20 and 150 atm.

[0026] Essence of a method according to a first alternative embodiment is the following.

[0027] While passing a solutions of LRWs and reagents required For the synthesis of compounds through a layer of insoluble particles in hydrothermal conditions, a new crystal phase is grown on layer forming particles, which represents the compounds immobilizing radionuclides.

[0028] One of the distinctions; of a method is the fact that in hydrothermal conditions, oxide synthesis is carried out by crystallization of a new phase on the surface of particles of layer, not in the volume of the layer, as in the case of a method known from patent RU 2185671,

[0029] Be it also noted that a composition of synthesizable compounds formable on the surface of particles can be different from the composition of particles of the layer and depends on the composition of an initial solution,

[0030] Essence of a method according to the second alternative embodiment is the following.

[0031] On passage of a solution of LRWs and reagents through a layer of oxides of insoluble particles in hydrothermal conditions, a new crystal phase is grown on layer-forming oxide particles, which represents the oxides immobilizing radionuclides,

[0032] One of the distinctions of a method is the fact that in hydrothermal conditions, oxide synthesis is performed through crystallization of a new phase on the surface of particles of a layer, not in the volume of the layer, as is the case with a known method (RU 2185671).

[0033] It should be noted that oxides appearing on the surface of oxides representing a layer of particles can differ as to a composition thereof from the oxides of the layer and are dependent on the composition of an initial solution.

[0034] Essence of a method according to the third alternative embodiment consists in the following.

[0035] While passing a solution of LRWs and reagents through a layer of insoluble oxides in hydrothermal conditions, a new crystal phase is grown on layer forming oxide particles, which represents the compounds immobilizing radionuclides.

[0036] One of the distinctions of a method is the fact that in hydrothermal conditions, the synthesis of insoluble particles is carried out through crystallization of a new phase on the surface of oxides of a layer, not in the volume of the layer, as in the case of a known method (RU 2185671).

[0037] The term "crystallization" as it understood here means the change of a substance from the liquid state to the solid crystal state and the term "crystallization on the surface of particles" is heterogenic formation of a crystal phase on the surface of a solid.

[0038] By the term "phase" in the context of the present invention one should imply a generally accepted in the art, uniform in formulatian and properties, part of a thermodynamic system separated from other phases by interfaces on which some of the properties of the system change stepwise,

[0039] By the term "immobilization" in the present invention one should imply inclusion of radionuclides in a crystal lattice of insoluble compounds crystallizable on the surface of particles of a layer.

[0040] During the realization of a process, a solution of LRW is passed through a layer of particles and on the surface of the layer in hydrothermal conditions, more exactly, at elevated temperature and pressure, now compounds are synthesized in form of crystals which immobilize radionuclides. The speed of passing of LRW solutions through the layer of particles should be such that the formation of crystals on the surface of the layer of immobilizing radionuclide particles provide the desirable degree of purification from the radionuclides. In the case the speed of a flow is greater than a certain value determined experimentally in each and every particular case there occurs crystallization in the volume of a solution but not the surface of particles of the layer and more than that a portion of radionuclides containing crystals arc lift out of the layer and no purification occurs whatsoever.

[0041] For purification to be carried out a solution being treated should contain ions forming under hydrothermal conditions the crystals of compounds immobilizing radionuclides- For the synthesis of a crystal phase reagents which would supply presence with ions required for the synthesis in the solution are added to the solution of LRW, said reagents being represented by oxidants such as hydrogen peroxide or potassium permanganate, oxidizing ions within the LRWs to an oxidation state of formation of insoluble compounds, and/or metal salts,

[0042] As a result of a research it has been established that crystal synthesis depends on the concrete conditions of a hydrothermal process. Thus, given the equal speed of a stream on initial solution which docs not exceed the speed of crystallization in a range of temperatures of from 180 to 250°C and pressure of from 20 to 150 atm, crystallization occurs on the surface of particles of a layer.

[0043] In case of a process being realized at a pressure of not less than 20 atm. and a temperature of below 180°C, crystallization partially occurs in a volume. A process carried out at a pressure of above 150 atm. and a temperature of above 250°C is not justified economically.

[0044] For details see for explanations of a process using diagrams in Figs, 1-3.

[0045] Fig. 1 shows the ASM-pictures of particles of a layer before hydrothermal synthesis (initial particle), Fig. 2- in the process of synthesis, Fig. 3- upon completion of hydrothermal synthesis.

Carrying out the Invention

[0046] A method for any one of the alternative embodiment is realized, as followings.

[0047] Reagents as required depending on the type of the LRWs being processed are added to the feeding LRW followed by feeding LRWs to the flow reactor for hydrothermal synthesis in which a layer of particles of insoluble compounds is placed.

[0048] Synthesis is carried out in a temperature range of 180 to 250°C, at a pressure of 20 to 150 atm., which corresponds to the sufficient rate of crystal growth and the desirable degree of purification from radionuclides.

[0049] The compounds resulting from hydrothermal synthesis are deposited on insoluble particles forming the layer.

[0050] Upon completion of a process, when all particles are covered by the crystals of synthesized compounds containing radionuclides, these are directed for storage or further treatment. A radionuclide-free solution is a process radioactive-free waste material.

Fig, 1 shows a process of purification during the initial time t. The speed of a LRW solution’s flow is sufficient for forming crystals on the surface of particles of a fixed layer.

Fig. 2 shows a process in a timed interval t’. A new crystal phase in the form of layered polycrystals has formed on the surface of particles forming the layer of insoluble particles. This corresponds to realization of the process for purification in the most favourable conditions.

Fig. 3 shows the process in final time t" when layered polycrystals with immobilized radionuclides have been formed on all the insoluble particles.

[0051] The layered structure of a synthesized compound which grows on an initial globular structure is seen on the pictures.

[0052] It has been found that the degree of purification from radionuclides during the synthesis of oxides was 10^2 to 10^4. A ratio of the volumes of LRWs being processed to the volume of the reactor partially filled with initial particles was 500-2000 or more, which fact corresponds to separation coefficients of more than 10^6.

[0053] The Invention is illustrated by the following examples.

[0054] EXAMPLE 1 (Variant 1). LRWs containing 2 g/l Trilon B and 0.5 g/l trisodium phosphate having a 0.1 g/l concentration of calcium ions and comprising strontium-90 radionuclides ($1.5 \cdot 10^{-6}$ Ci/l) are passed through a layer of hydroxylapatite Ca_3PO_4-$Ca(OH)_2$ having a particle size of 0.1-0.3 mm, charged into a healed cylindrical reactor dimensioned 100 x 10 mm. The process is carried out at the flow speed of I ml/min., at the temperature of 200°C and pressure of 100 atm. A solution flow is provided with a chromatographic high pressure pump. Simultaneously 6% hydrogen peroxide solution is added to the reactor by the high pressure pump at the rate of 0.6 ml/min. Activity of the effluent solution and the leaching coefficients of strontium radionuclides from the layer of hydroxylapatite with synthesized calcium phosphate polycrystals which immobilized the radionuclides (charge), as specified upon completion of a test are given in Table 1

Table 1

Solution, volume, ml	Strontium-90, activity, Ci/l
100	$1 \cdot 10^{-10}$
500	$6{,}7 \cdot 10^{-10}$
1000	$1{,}9 \cdot 10^{-9}$
2500	$4{,}1 \cdot 10^{-8}$
Leaching coefficient for charge, g/cm^2-day	$1 \cdot 10^{-5}$

[0055] EXAMPLE 2 (Variant 2). The bottoms of a nuclear waste evaporators which arc purified from cesium radionuclides by filtration through ferrocyanide sorbets and contained cobalt-60 radionuclides ($1 \cdot 10^{-5}$ Cl/l) and manganese-54 ($1 \cdot 10^{-8}$ Ci/l) arc passed through a layer of iron-cobalt ferrite (iron-cobalt oxides) with an iron to cobalt molar ratio of 1: 01 and a particle size of 0.2-0.5 mm charged into a heated cylindrical reactor dimensioned 100 x10 mm. The process is carried out at the flow speed of 2 ml/min., at the temperature of 220°C and pressure of 100 atm. A solution flow is provided with a high pressure chromatographic pump. Simultaneously 6% solution of hydrogen peroxide is added to the reactor by the second high pressure pump at the rate of 0.6 ml/min. Activity of the effluent solution and the leaching coefficients of cobalt radionuclides from the charge of oxides formed, as specified upon completion of a test arc given in Table 2.

Table 2

Solution, volume, ml	Cobalt-60, activity, Ci/l	Manganese-54, activity, Ci/l
100	$1{,}4 \cdot 10^{-9}$	$<1 \cdot 10^{-11}$
500	$1{,}1 \cdot 10^{-9}$	$<1 \cdot 10^{-11}$
1000	$1{,}7 \cdot 10^{-9}$	$<1 \cdot 10^{-11}$
2500	$1{,}5 \cdot 10^{-9}$	$<1 \cdot 10^{-11}$
5000	$2{,}1 \cdot 10^{-11}$	$<1 \cdot 10^{-11}$
Leaching coefficient for charged, g/cm^2 day	$2 \cdot 10^{-8}$	$<1 \cdot 10^{-7}$

[0056] EXAMPLE 3 (Variant 3). LRWs containing 2 g/l Trilon B and 0.5 g/l trisodium phosphate having a concentration of calcium ions of 0,1 g/l and comprising strontium-90 radionuclides ($1.5 \cdot 10^{-6}$ Ci/l) are passed through a layer of zirconium oxide having a particle size of 0.1-0.3 mm, charged into a heated cylindrical reactor dimensioned 100 x 10 mm. The process proceeds al the speed of a flow of 1 ml/min., at 200°C and the pressure of 100 atm. A section flow is provided with a chlomatographic high pressure pump. Simultaneously 6% solution of hydrogen peroxide is added to the reactor by a high pressure pump at the rate of 0.6 ml/min. Activity of an effluent solution and the leaching coefficients of strontium radionuclides from the charge of calcium phosphides and zirconium, as specified upon completion of a test are given in Table 3.

Table 3

Solution, volume, ml	Activity, strontium-90, Ci/l
100	$1\cdot10^{-10}$
500	$1,8\cdot10^{-9}$
1000	$2,1\cdot10^{-8}$
Leaching coefficient for charge, g/cm^2 day	$6\cdot10^{-5}$

[0057] EXAMPLE 4. Sea water contaminated with strontium-90 radionuclides, $2\cdot10^{-6}$ Ci Activity, is passed through a layer of manganese dioxide having a particle size of 0.05-0.1 mm, charged in a heated cylindrical reactor dimensioned 100 x 10 mm. The process is carried out at the speed of a flow of 1 ml/min. at 220°C and the pressure of 100 atm. A solution flow is provided with a high pressure chromatographic pump. A solution 0.1 n manganese (II) chloride and 0.1 n potassium permanganate solution were added to the reactor by high pressure pumps at the rate of 0.6 ml/min. Activity of an effluent solution and the the leaching coefficients of strontium radionuclides from a charge of formable oxides as specified upon completion of a test are shown in Table 4

Table 4

Solution, volume, ml	Activity, strontium-90, Ci/l
100	$5,6\cdot10^{-9}$
500	$4,0\cdot10^{-9}$
1000	$4,3\cdot10^{-9}$
1500	$4,5\cdot10^{-9}$
2000	$5,\cdot10^{-9}$
Leaching coefficient for charge, g/cm^2 day	$1,4-10^{-7}$

[0058] EXAMPLE 5. LRWs being decontaminated containing 2 g/l sodium oxalate and 0.5 g/l Trilon B purified from cesium radionuclides by filtration through ferrocyanide sorbents and comprising cobalt 60 ($1-10^{-7}$ Ci/l) and strontium-90 ($4\cdot10^{-7}$ Ci/l) radionuclides are successively passed though a layer of iron-cobalt ferrite with a molar ratio of iron: cobalt of 1: 0.1 and a particle size of 0.2-0.5 mm, charged in a heated cylindrical reactor dimensioned 100 x 10 mm and through a layer of manganese dioxide having a particle size of 0.05-0.1 mm, charged in the heated cylindrical reactor dimensioned 100 x 10 mm. The process proceeds at the speed of a flow of 1 ml/min, at 200°C and pressure of 100 bar. A solution flow is provided a high pressure chromatographic pump. Simultaneously 6% hydrogen peroxide solution at the rate of 0.6 ml/min is added to the first reactor and 0.1 n manganese (II) chloride solution is added to the second reactor by the high-pressure pump. Activity of an effluent solution and the leaching coefficients of cobalt radionuclides from formable oxides as specified upon completion of a test are shown in Table 5

Table 5

Solution, volume, ml	Activity, cobalt-60, Ci/l	Activity, strontium-90, Ci/l
100	$< 1\cdot10^{-11}$	$1\cdot10^{-10}$
500	$< 1\cdot10^{-11}$	$1,4\cdot10^{-10}$
1000	$< 1\cdot10^{-11}$	$2,7\cdot10^{-10}$
2500	$< 1\cdot10^{-11}$	$1\cdot10^{-10}$
5000	$< 1\cdot10^{-11}$	$4.3\cdot10^{-9}$
Leaching coefficient for charge, g/cm$^2\cdot$day	$2\cdot10^{-8}$	$3\cdot10^{-7}$

[0059] EXAMPLE 6. Alkali LRWs containing 0.3 g/l sodium hydroxide cobalt-60 ($1 \cdot 10^{-7}$ Ci/l) and cesium - 137 ($6 \cdot 10^{-7}$ Ci/l) radionuclides are passed through a layer of perlite-filter with the contained 3.4% iron, charged in a heated cylindrical reactor dimensioned 100 x 10 mm. The process is conduced at the speed of a flow of 0.3 ml/min. at 170°C and the pressure of 100 atm. A solution flow is provided with the high pressure chromatographic pump. Activity of an effluent solution and the leaching coefficients of cobalt/cesium radionuclides from a charge of combined iron oxides and alumosilicates (faujasite in the main) as specified upon completion of a test are shown in Table 6,

Table 6

Solution, volume, ml	Activity, cobalt-60, Ci/l	Activity, cesium-137, Ci/l
100	$7.4 \cdot 10^{-10}$	$2,1 \cdot 10^{-9}$
200	$2,1 \cdot 10^{-10}$	$7,8 \cdot 10^{-10}$
500	$4,2 \cdot 10^{-10}$	$1,1 \cdot 10^{-9}$
800	$7,9 \cdot 10^{-10}$	$1 \cdot 10^{-9}$
1000	$1,1 \cdot 10^{-8}$	$5,4 \cdot 10^{-8}$
Leaching coefficient for charge, g/cm^2·day	$1 \cdot 10^{-6}$	$1 \cdot 10^{-5}$
Leaching coefficient for cement stone, g/cm^2-day	$5 \cdot 10^{-4}$	$5 \cdot 10^{-4}$

[0060] The afore-cited experimental data go to show that in treatment of LRWs by methods as claimed a charge representing either metal salts or metal oxides with immobilized storage suitable radionuclides is forming. A degree of leaching radionuclides is about $10^{-5} \cdot 10^{-7}$ g/cm^2. day. The formed solutions are non-radioactive factory wastes.

Claims

1. A method of reprocessing liquid radioactive wastes (LRW) containing long-lived radionuclides by synthesis of insoluble compounds immobilizing the long-lived radionuclides, **characterized in that** the synthesis of insoluble compounds is carried out in hydrothermal conditions in a flow by passing the LRWs being processed and reagents required for the synthesis through a layer of insoluble particles at a rate providing for recrystallizing synthesizable compounds containing radionuclides on the surface of particles of the layer.

2. The method according to claim 1, **characterized in that** said particles are metal oxides or salts.

3. The method according to claim 2, **characterized in that** said metal oxides arc iron oxide and/or manganese oxide and/or cobalt oxide and the salt is hydroxylapatite.

4. The method according to claim 1, **characterized in that** the hydrothermal synthesis is carried out at a temperature range from 180°C to 250°C and a pressure range from 20 to 150 atm.

5. A method of reprocessing liquid radioactive waste (LRW) containing long-lived radionuclides by the synthesis of insoluble compounds immobilizing long-lived radionuclides into a crystal lattice, **characterized in that** a crystal phase is synthesized as oxides in hydrothermal conditions in a flow by passing LRWs being processed and reagents required for the synthesis through a layer of metal oxides at a rate providing for crystallizing synthesizable radionuclide-containing oxides on the surface of the particles of a layer of oxides.

6. The method according to claim 5, **characterized in that** said metal oxides are iron oxide and/or manganese oxide and/or cobalt oxide and/or zirconium oxide.

7. The method according to claim 6, **characterized in that** hydrothermal synthesis is carried out at a temperature range from 180°C to 250°C and a pressure range from 20 to 150 atm.

8. A method of reprocessing liquid radioactive waste (LRW) containing long-lived radionuclides by the synthesis of Soluble compounds immobilizing long-lived radionuclides into a crystal lattice, **characterized in that** the synthesis of a crystal phase is carried out in hydrothermal conditions in a flow by passing LRWs being processed and reagents required for synthesis through a layer of metal oxides at a rate providing for crystallizing of synthesizable radionuclide-containing compounds on the surface of the particles of a layer of oxides.

9. The method according to claim 8, **characterized in that** said metal oxides are iron oxide and/or manganese oxide and/or cobalt oxide and/or zirconium oxide.

10. The method according to claim 9, **characterized in that** hydrothermal synthesis is carried out at a temperature range from 180°C. and 250°C and a pressure range from 20 to 150 atm.

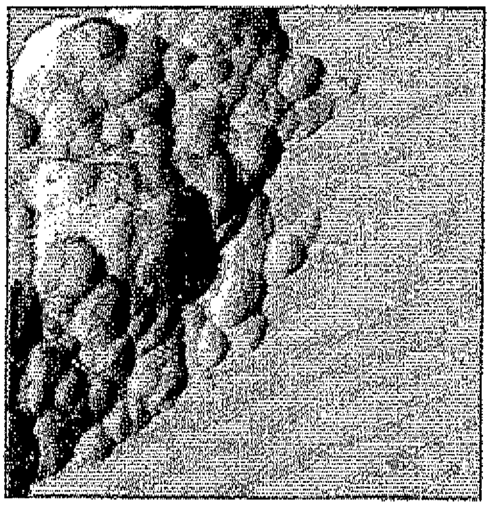

Fig.1

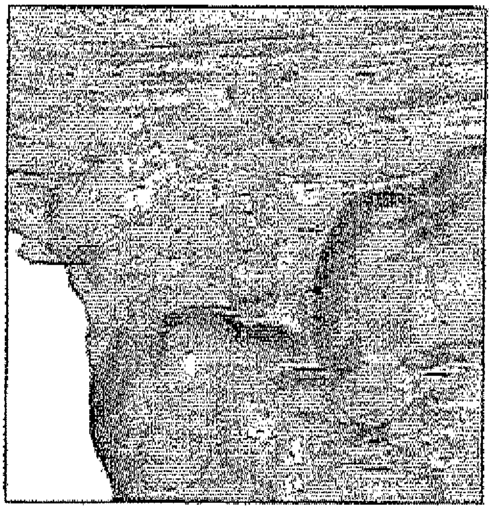

Fig.2

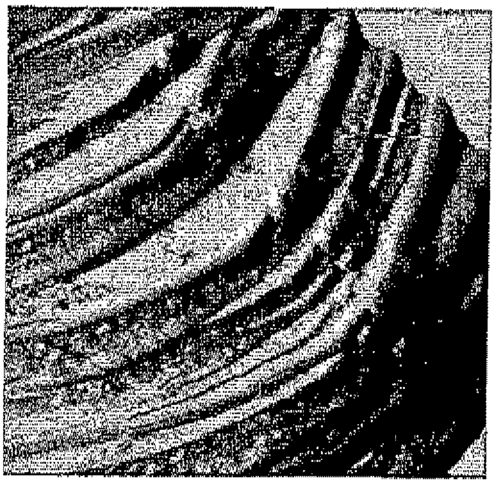

Fig.3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 2007/000614

A. CLASSIFICATION OF SUBJECT MATTER *G21F 9/16 (2006.01)*

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

G21F 9/00, 9/04, 9/06, 9/16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

RUPAT, Esp@cenet, USPTO DB, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	RU 2185671 C1 (GOSUDARSTVENNOE UCHREZHDENIE-INSTITUT KHIMII DALNEVOSTOCHNOGO OTDELENIYA RAN) 20.07.2002, the abstract	1-10
A	RU 2212069 C2 (PROIZVODSTVENNOE OBEDINENIE "MAYAK") 10.09.2003, the abstract	1-10
A	DE 3833676 A1 (PETRI, JURGEN) 05.04.1990, the abstract	1-10
A	JP 6-160593 A (TOKYO SHIBAURA ELECTRIC CO et al.) 07.06.1994, the abstract	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- RU N2088986 **[0002]**
- RU N2271586 **[0002]**
- RU N2131152 **[0002]**
- RU N2153717 **[0005]**
- EP N0007236 A **[0005]**
- US N4274976 A **[0005]**
- RU N2185671 **[0013]**
- RU 2185671 **[0028] [0032] [0036]**

Non-patent literature cited in the description

- **Donald I.W. ; Metcalfe B.L. ; Taylor R.N.J.** immobilization of high level radioactive wastes using ceramics and glasses. Review. *Journal of Materials Science,* 1997, vol. 32, 5856-5862 **[0002]**
- **Ringwood A.E. ; Kesson S.E. ; Reeve K.D. ; Levins D.M. ; Ramm E.J.** Synroc. In: Radioactive Waste Forms for the Future. Elsevier Science Publishers B.V, 1988, 233-334 **[0005]**
- **Donald I.W. ; Metcalfe B.L. ; Taylor R.N.J.** The immobilisation of high level radioactive wastes, using ceramic and glasses. Review. *Journal of Materials Science,* 1997, vol. 32, 5862-5865 **[0005]**
- **Johnson CD. ; Skakle J.M. S. ; Johnson M.G ; Feldmann J. ; Macphee D.E.** Hydrothermal synthesis, crystal structure and acqueous stability of two cadmium arsenate phases, CdNH4(HAsO4)OH and Cd5H2(AsO4)4-4H2O. *J. Mater.Chem.,* 2003, vol. 13, 1429-1432 **[0009]**