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(54) **METHOD FOR REPROCESSING LIQUID RADIOACTIVE WASTE**

(57) The invention relates to the technology of liquid radioactive waste (LRW) treatment. The method for liquid radioactive waste treatment includes filtering, liquid radioactive waste oxidizing to produce an oxidized stream, its filtering, microfiltration and purification from radionuclides by feeding the filtrate into a container with granular selective sorbents. After oxidation, selective sorbent is

introduced into the oxidized stream before filtering, and the sorbent is introduced into the liquid radioactive waste only after the oxidation stage.

The invention makes it possible to increase the effectiveness of the LRW treatment method by reducing the volume of radioactive waste requiring special storage. 2 ex.

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Description

[0001] The invention relates to a liquid radioactive waste (LRW) treatment technology and can be used for processing of radioactive substances at various nuclear industry facilities.

[0002] This method can be used at various nuclear industry facilities, including nuclear power plants, for low-level and intermediate-level LRW treatment, for treatment of solutions generated during decontamination of buildings, structures, equipment, vehicles etc., for treatment of natural water contaminated with radionuclides.

[0003] LRW treatment is aimed at solving two main problems: purifying the bulk of the waste from radionuclides and concentrating the latter in a minimal volume.

[0004] There is a method of nuclear power plants LRW treatment, which involves ozonation of saline waste and subsequent separation of radioactive sludge generated during oxidation (Invention patent of the Russian Federation No2066493 "Method for treatment of liquid radioactive waste of nuclear power plants", ⁶ IPC G21F 9/08, priority date 13/11/1995, published 10/09/1996)

[0005] Disadvantages of the method include low coefficients of purification from radionuclides remaining in the liquid phase after oxidation in the ionic state, namely, from radionuclides of caesium.

[0006] There is a method for treatment of LRW containing radionuclides in ionic and colloidal forms and ballast components of mineral and organic nature in dissolved and suspended states. Organic components of liquid radioactive waste are oxidized to a gaseous state, and mineral ionic components, including radionuclides, are suspended in the form of metal hydroxides by supplying ozone into the flow of waste. The flow of oxidized waste is separated into a condensed sludge and a liquid phase. Selective sorbents are used for further purification of the liquid phase from the radionuclides remaining in the ionic form. Resulting sludge and spent sorbents are converted into a solid form and sent for long-term storage (Invention patent of the Russian Federation No2122753 "Method for treatment of liquid waste containing radionuclides", ⁶ IPC G21F 9/06, priority date 30/10/1997, published 27/11/1998).

[0007] Disadvantage of the method is that there is no guarantee of full ozone saturation of the liquid under conditions of the flow treatment. This leads to the slip of the complex form of radionuclides into the purified liquid phase through a selective sorbent, because neither separation of condensed sludge nor selective sorption can trap out complex radionuclides, that reduces overall LRW treatment effectiveness.

[0008] There is a method for treatment of LRW containing radionuclides in ionic and colloidal forms and ballast components of mineral and organic nature in dissolved and suspended states. Organic components of liquid radioactive waste are oxidized to a gaseous state, and mineral ionic components, including radionuclides, are suspended in the form of metal hydroxides by sup-

plying ozone into the flow of waste. The flow of oxidized waste is separated into a condensed sludge and a liquid phase. Selective sorbents are used for further purification of the liquid phase from the radionuclides remaining in the ionic form. Resulting sludge and spent sorbents are converted into a solid form and sent for long-term storage. The waste flow is purified from suspended particles by filtration on a mesh filter material before ozone treatment. Ozone treatment is carried out in a circulating mode. The oxidized flow is separated to a condensed sludge and a liquid phase by filtration on a mesh filter material. before purification of the liquid phase with selective sorbents Membrane microfiltration is carried out to separate the liquid phase from radionuclides in colloidal form to return them to the stream of liquid radioactive waste after ozone is applied (Invention patent of the Russian Federation No2268513 "Method for liquid radioactive waste treatment", ⁷ IPC G21F 9/06, G21F 9/20, priority date 28/12/2004, published 20/01/2006).

[0009] The main disadvantage of this method is that caesium radionuclides in ionic form contributing the most to the total activity of LRW are removed only at the final stage of the process - by selective sorbents placed in filter containers. Thus, when initial activity of caesium radionuclides in LRW is 3.7×10^8 Bq/l (10 Ci/m³), no more than 12 m³ LRW can be passed through a filter container with granular selective sorbent based on nickel ferrocyanide, since the filter container capacity is 120 Ci in terms of the accumulated radioactivity (see http://nii-izoterm.ru/index.php?option=com_content&task=view&id=72&Itemid=51).

In real conditions at a nuclear power plant the bottoms contain from 3 to 10 Ci/m³ after LRW evaporation. Therefore, at least 55 expensive filter containers of complex design are needed to process 1,000 m³ of such LRW using the prototype method. (The cost of one filter container, taking into account its installation and operation, is about 2 million roubles). In addition, due to high activity accumulated in each used filter container (up to 120 Ci in terms of Cs-137), its movement, maintenance and storage are very difficult and expensive, as special measures are necessary to protect personnel from radiation. To store this quantity of filter containers (55 pieces per 1,000 m³ of LRW) according to technological requirements, a special at least 100 m³ repository is necessary. Thus, the effective volume reduction factor of 1,000 m³ of LRW treatment will be no more than 10.

[0010] As a prototype, we consider a method of liquid radioactive waste processing and disposal, including oxidation of waste, separation of sludge, colloids and suspended particles from the liquid phase and removal of radionuclides from the liquid phase for subsequent disposal using selective sorbents and filters. The method is characterised by the following. Before the stage of separating sludge, colloids and suspended particles from the liquid phase of the radioactive waste, selective sorbents in the form of powders are added to them with stirring. Then the resulting suspension is filtered, pumping

through at least one container designed for waste disposal and equipped with at least one filter element at the outlet that separates insoluble substances from the liquid phase. After that, the filtrate is passed through at least one container designed for waste disposal with granular selective sorbents. These containers are placed in concrete blocks.

[0011] Implementation example: the above mentioned method was used for treatment of LRW (pH 12.1) containing:

- dry residue (after drying at 105 °C) 285 g / l;
- suspended solids (separated on the blue ribbon filter) 5.1 g / l;
- activity of caesium-137: 1.1×10^{-3} Ci / l;
- activity of cobalt-60: 1.4×10^{-6} Ci / l.

[0012] 5 m³ of this LRW was pumped into a tank. Composition consisting of 5 kg of selective Nickel ferrocyanide sorbent applied to the powder of amorphous silicon dioxide from Sukhoy Log field with a particle size from 200 to 500 μm and 0.5 kg of nickel sulphate as a coagulant was added with stirring. Combination of amorphous silica and agglomerates formed by interaction of the nickel-based coagulant and suspended LRW particles makes it easy to separate the solid phase from the liquid inside a Corebrick F.

[0013] After 2 hours of stirring, the suspension consisting of the sorbent, suspended particles from the LRW and the coagulant was fed to Corebrick F (position 2) with two filter elements, and after that the solution purified from the suspension was sent to ozonation (position 3) to destroy organic compounds and complexes. 5 kg of the same sorbent as in the tank (position 1) was added to the suspension formed during oxidation, and the resulting suspension was sent to Corebrick F (position 4) with two filter elements. The solution purified from suspension was passed through Corebricks C (positions 5 and 6) connected in series with granular selective sorbent based on nickel ferrocyanide. The purified solution containing less than 10 Bq / l of Cs-137 and Co-60 was sent for evaporation and crystallisation, (see Invention patent of the Russian Federation №2577512 "Method for treatment of liquid radioactive waste and its disposal", priority date 29/12/2014, published 20/03/2016)

[0014] The main disadvantage of the prototype is that using the sorbent before ozonation lets trace amounts of transition metals included in the sorbent enter the ozonation system after filtration, and catalytically destroy ozone. This leads to a significant decrease in the efficiency of ozonation, an increase in the time of ozonation, and, in some cases, to inability to purify LRW from a number of radionuclides.

[0015] Technical result of the claimed invention is to increase effectiveness of the method by reducing the volume of radioactive waste requiring special storage and to reduce the dose of radiation exposure of the staff during the LRW treatment.

[0016] The claimed technical result is achieved by the fact that the LRW treatment method includes filtration, oxidation of LRW to obtain an oxidized flow, its filtration, microfiltration and purification from radionuclides by supplying the filtrate into a container with granular selective sorbents. Moreover, after oxidation, a selective sorbent is added to the oxidized stream before filtration, and the sorbent is added to the LRW only after the oxidation stage.

[0017] The novelty of the claimed invention consists in the addition of the sorbent to the liquid radioactive waste only after the stage of oxidation.

[0018] When using a sorbent before oxidation (as in the prototype method), trace amounts of transition metals included in the sorbent enter the ozonation system after filtration, and catalytically destroy ozone. This leads to a significant decrease in the efficiency of ozonation, an increase in the time of ozonation, and, in some cases, to inability to purify LRW from a number of radionuclides. At the same time, the effectiveness of using sorbents after the ozonation is 40-70% higher than before the ozonation. Therefore, a significant reduction in the amount of sorbents supplied and the volume of spent radioactive sorbents sent for disposal is achieved. We exclude equipment for feeding the sorbent before the ozonation stage, like tanks, pumps, pipelines, etc., which in the case of a breakdown also becomes a radioactive waste and requires disposal.

[0019] Thus, the addition of the sorbent to the LRW only after the oxidation stage leads to the decrease in the volume of radioactive waste requiring special storage.

[0020] One or more selective sorbents are added to the oxidized stream during the LRW treatment.

[0021] The selective sorbent is introduced into the oxidized stream in the form of a paste or suspension, or in the form of a powder, or in the form of granules

[0022] Adding a selective sorbent after oxidation to the oxidized flow before filtration makes it possible to transfer the main amount of radionuclides, including caesium radionuclides, to the sludge that is separated at the filtration and microfiltration stages. At the same time, the activity of caesium radionuclides in the liquid phase after filtration decreases to 10^{-4} - 10^{-5} Ci/m³. Therefore one filter container can be used to treat not 12 m³, as in the analogue method, but up to 10,000 m³ of LRW. Accordingly, the effective waste volume reduction factor will increase to at least 100. The number of expensive filter containers required for LRW processing and the costs of their special storage will also decrease by at least 100 times. At the same time, addition of the selective sorbent will increase the waste volume insignificantly compared to the initial volume of LRW, and this waste will not be sent for special storage, but will be conditioned in normal mode using conventional cementing technology and buried, and it is crucial.

[0023] No technical solution that coincides with the set of significant features of the claimed invention has been

detected. This allows us to conclude that the claimed invention meets the "novelty" eligibility criterion.

[0024] The claimed significant features that predetermine the specified technical result, do not obviously ensue from the prior art. This allows us to conclude that the claimed invention meets the "inventiveness" patentability criterion.

[0025] "Industrial applicability" is proved by examples of practical implementation of the claimed method presented below.

Example 1

[0026] The method was applied for treatment of LRW of the following composition: pH = 10.2; total salt content of 371 g/l; activity in terms of Cs-137 - 12.16 Ci/m³ (1.2×10^{-2} Ci/l); in terms of Co-60 - 0.09 Ci/m³ (9×10^{-5} Ci/l).

[0027] 30 g (0.3% of LRW weight) of a caesium selective sorbent based on nickel ferrocyanide with a particle size of 100 μ m were added to 10 litres of initial LRW, which, after preliminary filtration on a mesh filter (particles larger than 50 μ m were separated) and ozonation, contained less than 10^{-9} Ci/l of Co-60 and 1.1×10^{-2} Ci/l of Cs-137. After 1 hour of stirring, the resulting suspension was first filtered on a mesh filter with fineness of less than 5 μ m, and then microfiltration on ceramic membranes with 0.2 μ m pores was carried out. The content of Cs-137 in the purified solution became 4.1×10^{-8} Ci/l. When processing such LRW, the resource of the filter container currently used at nuclear power plants will be at least 1,000 m³. If there is no stage of applying the powder sorbent, the Cs-137 content in the purified solution will be 1.1×10^{-2} Ci/l, and the resource of the filter container will be less than 10 m³ of LRW.

Example 2

[0028] 100 g of an aqueous suspension of nickel ferrocyanide sorbent (containing 50 g (0.5% of LRW weight) of the colloidal nickel ferrocyanide sorbent) were added to the same LRW as in Example 1 after ozonation. The solution was filtered after two hours of stirring likewise. The activity of the solution became lower than 0.4×10^{-10} Ci/l. Based on radiation safety standards, such a solution does not require further purification using filter containers. After evaporation of the solution, the resulting melt can be stored in landfills with non-radioactive chemical materials.

Claims

1. A method for liquid radioactive waste treatment, comprising filtering, liquid radioactive waste oxidizing to produce an oxidized stream, its filtering, microfiltration and purification from radionuclides by feeding the filtrate into a container with granular selective sorbents. The method is different from the

prior art in that after oxidation, selective sorbent is introduced into the oxidized stream before filtering, and the sorbent is introduced into the liquid radioactive waste only after the stage of oxidation.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/RU 2018/000831

5	A. CLASSIFICATION OF SUBJECT MATTER	
	G21F 9/04 (2006.01)	
	According to International Patent Classification (IPC) or to both national classification and IPC	
	B. FIELDS SEARCHED	
10	Minimum documentation searched (classification system followed by classification symbols)	
	G21F 9/00, 9/04, 9/06, 9/12, 9/16	
	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched	
15	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)	
	PatSearch (RUPTO internal), USPTO, PAJ, Esp@cenet, Information Retrieval System of FIPS	
20	C. DOCUMENTS CONSIDERED TO BE RELEVANT	
	Category*	Citation of document, with indication, where appropriate, of the relevant passages
		Relevant to claim No.
25	D, A	RU 2577512 C2 (OBSCHESTVO S OGRANICHENNOM OTVETSTVENNOSTJU "NAUCHNO-PROIZVODSTVENNOE PREDPRIYATIE "EKSORB") 20.03.2016
	A	RU 2473145 C1 (ROSSYSKAYA FEDERATSIA, OT IMENI KOTOROI VYSTUPAET GOSUDARSTVENNAYA KORPORATSIA PO ATOMNOI ENERGII "ROSATOM" et al.) 20.01.2013
30	A	RU 2256965 C2 (FGUP "PROIZVODSTVENNOE OBEDINENIE "MAYAK") 20.07.2005
	A	RU 2131627 C1 (PROIZVODSTVENNOE OBEDINENIE "MAYAK") 10.06.1999
35	A	US 5960368 A (WESTINGHOUSE SAVANNAH RIVER COMPANY) 28.09.1999
40	☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.	
45	* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "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 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
50	Date of the actual completion of the international search	Date of mailing of the international search report
	09 April 2019 (09.04.2019)	25 April 2019 (25.04.2019)
	Name and mailing address of the ISA/ RU	Authorized officer
55	Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2066493 A [0004]
- WO 2122753 A [0006]
- WO 2268513 A [0008]
- WO 2577512 A [0013]