

Sorption Technology for Deactivation of Salty Liquid Radioactive Waste and the Prospects of Its Application to Rehabilitate Polluted Territories

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Abstract

Outlook for application of amorphous sorbents on the basis of titanyl hydrophosphate to decontaminate liquid radioactive wastes from ^{137}Cs , ^{134}Cs , ^{90}Sr , and ^{60}Co radionuclides with elevated (up to 32 g/l) salt background that corresponds in composition to sea water has been shown. Impurities in the form of petroleum derivatives (up to 0.4 g/l) and solid suspensions have no considerable effect on the deactivation and they can be separated together with the waste sorbent from the being cleared solution. The flow chart for the decontamination has been suggested. Heat treatment of the waste sorbent enables conducting immobilization of radionuclides within a solid phase. A variant of deactivation of soils that are polluted by radionuclides has been suggested.

INTRODUCTION

When transport nuclear power units are in operation, liquid radioactive wastes (LRW) on the basis of sea water are formed with the specific activity of 10^2 – 10^7 Bq/l that is controlled by the presence of ^{137}Cs , ^{134}Cs , ^{90}Sr , and ^{60}Co radionuclides [1]. These LRW contain suspensions and petroleum derivatives [1], together with significant amount of cations of non-radioactive alkaline and alkaline-earth elements ($\text{Li} \leq 0.2$, $\text{Rb} \leq 0.12$, $\text{Sr} \text{ 8–13 mg/l}$, $\text{Na} \leq 10.5$, $\text{K} \leq 0.38$, $\text{Mg} \leq 1.35$, $\text{Ca} \leq 0.4$ g/l [2]), which tangibly complicates their deactivation.

Liquid radioactive wastes with a low content of non-radioactive salts (0.02–0.07 g/l) are deactivated by sorption methods with the use of ion-exchange resins or with a complex of granular selective inorganic sorbents [3]. These methods are ineffective for salty LRW in view of a high content of non-radioactive cations of strontium and alkaline and alkaline-earth elements with close chemical properties and in view of water-insoluble products of the

equipment corrosion (suspended solids) and petroleum derivatives (up to 3–5 mg/l). To take an example, the content of the last-mentioned in an interval of 0.07–0.09 mg/l leads to a 62% fall in dynamic exchange capacity of a granular sorbent [4]. Decontamination schemes for LRW with a medium content of non-radioactive salts (6–8 g/l) are complex, expensive, and insufficiently effective. Accordingly, it has been suggested to conduct a primary defecation of the solution by the procedure of electrochemical contact coagulation that includes catalytic oxidation of the evolving hydrogen, a two-stage filtering of the being cleared solution by means of a mechanical filter, and removal of the dissolved forms of the radionuclides with the use of two selective sorbents [3]. However, this technology requires the application of numerous equipments, and the radioactivity “dissipates” over a number of products.

With alternative approach, LRW that incorporates 5–8 g/l of non-radioactive salts is concentrated by means of osmosis after a prior filtration [5], which results in a filtrate with

a low content of salts and radionuclides and a brine (~1/4 of the initial volume) that concentrates the basic part of radionuclides, and the content of salts amounts to 20–30 g/l. The filtrate after two-stage sorption decontamination meets sanitary standards. However, there is no deactivation technology for the formed brine.

Hence, LRW from transport nuclear power units with a higher than usual content of salts are not deactivated, and they are accumulated in coastal reservoirs, thus creating a hazard of radioactive pollution of the nearby territories and water surfaces [6].

To decontaminate LRW by means of sorption, inorganic sorbents can be used [7] that can outperform ion-exchange resins for their sorption characteristics, especially for selectivity [8]. The researches that are published in the last decades have demonstrated that to solve the problem under discussion, sorbents based on ferrocyanides of *d*-elements (for example, those of copper, nickel, and titanium), manganese oxides, phosphates of multivalent metals (tin, titanium, and zirconium), as well as synthetic zeolites hold promise. Efforts of researchers are aimed to survey and to study crystalline materials with easily reproducible properties [9]. The listed materials are characterized by good sorption properties, but they show various disadvantages. Accordingly, ferrocyanides (for example, a Thermoxide-12 type sorbent) effectively sorb cesium radionuclides alone. Sorbents of this class are unstable, which complicates the subsequent burial of sorbents sated by radionuclides. Of the sorbents that are produced in Russia, an ISMA-3 type sorbent that represents a modified manganese dioxide of $\text{Na}_{0.06-0.08}\text{Sr}_{0.11-0.12}\text{MnO}_{1.94-1.95}\cdot 0.025\text{Al}_2\text{O}_3\cdot(0.6-0.7)\text{H}_2\text{O}$ formulation is most effective for the selective extraction of strontium cations from solutions. Its sorption capacity for strontium is low and it is 0.18–0.34 mg-eq/g (8–15 mg/g), and the separation factor $K_{\text{Sr}/\text{Ca}} = 23$. However, the mentioned materials are expensive and they require a complicated treatment to transform them into chemical speciation that is suitable for storage, and when used for deactivation of LRW with an elevated salt background, their efficiency drops considerably. The existing approaches to obtain granular sorbents based on phosphates of transition elements (for

example, Thermoxide-3A) are complicated; they require much resource and often give rise to materials with the properties difficult to reproduce. Titanosilicates [10, 11] are effective among zeolites; however, application of the material for LRW deactivation is unacceptable because of its high cost (~\$200/kg) that is determined by a sophisticated production technology [12].

This contribution summarizes the results of investigations into the development of an effective procedure to decontaminate LRW from transport nuclear power units with an elevated (up to 32 g/l) salt background that matches sea water in its composition.

EXPERIMENTAL

Sorbents based on titanyl hydrophosphate ($\text{TiOHPO}_4 \cdot n\text{H}_2\text{O}$) that have been obtained by precipitation from sulphate solutions or by treatment of titanium hydroxide (IV) with orthophosphoric acid solution [13–15] were used in this work. Composition of the synthesized phosphate compounds of titanium (IV) were analysed photocolometrically for titanium (IV) and phosphorus (V) content with hydrogen peroxide and ammonium molybdate respectively. Water content was determined by thermogravimetric method. The developed methods of sorbent synthesis made it possible to obtain powdered and granular products [14, 15].

Sorption process in model chloride solutions was studied based on the pH variation of the aqueous slurry *versus* its composition upon heterogeneous replacement of hydrogen ions in titanyl hydrophosphate by cations of the appropriate alkaline or alkaline-earth metal (Li, Na, K, Rb, Cs, Mg, Ca, Sr or Ba). Time-stationary pH values with an accuracy of ± 0.02 that were generated with the use of I-130.2M.1 ionomer were taken as equilibrium values. An ESL-43-07 type electrode that was selective for hydrogen ions with coordinates of the isopotential point pH_i that were equal to $7 \pm 0.3 \text{pH}$ served as an indicator electrode, and an EVL-1M3 type silver-chloride electrode ($\text{Ag}|\text{AgCl}$, sat. KCl solution), the potential of which relative to normal hydrogen electrode at 20 °C measures (202 ± 2) mV, has been chosen

as an auxiliary electrode. Equilibrium concentration and activity coefficient of hydrogen ions were found from a calibrating function $\text{pH}-C_{\text{H}^+}$ with the appropriate constant values of ionic strength of the solution, and from literary data as well.

The content of sorbed cations of metal within the samples of a solid phase was additionally determined by a flame photometry method.

Hydrolytic stability of sorbents was studied in an interval of concentrations of a solid phase in aqueous slurries of 0.003–0.075 mol/l. The hydrolysis degree β was determined as

$$\beta = (C_{\text{H}_3\text{PO}_4}/C_{\text{TiOHPO}_4}) \cdot 100 \% \quad (1)$$

where $C_{\text{H}_3\text{PO}_4}$ was the quantity of H_3PO_4 in filtrates from the hydrolysed suspensions, and C_{TiOHPO_4} was the quantity of TiOHPO_4 in an initial sorbent.

Differential thermal analysis of solid phases was conducted with the use of a low-frequency NTR-70 thermographic recording unit with the programmed heating unit PRT-1000M. A sample of calcinated Al_2O_3 was used as the reference substance. Thermogravimetric analysis of a solid phase was conducted by means of tensor balance VT-1000. A temperature was determined with platinum *versus* platinum/rhodium thermocouples equipped with a PP-63 potentiometer. Measurements were conducted in quartz sample pans. The heating rate comprised 10 °C/min.

LRW with the respective γ - and β -activity being equal to $1.6 \cdot 10^5$ and $4.8 \cdot 10^4$ Bq/kg were used as initial real processing media. The initial LRW samples contained 32 g/l of salts in addition to radionuclides, the salts matching diluted sea water in the elemental ratio, and 2.0 g/l of suspensions that were composed of corrosion products of metal equipment (mostly of iron hydroxide). By virtue of the fact that LRW processing media may contain petroleum derivatives, ≈ 0.04 mass % of petroleum derivatives were additionally introduced in particular experiments.

Sorption deactivation of LRW was studied by radiometric methods. A weighted sample of a sorbent was introduced into an intensively stirred test sample; after a certain time, the solution was separated by filtering or by centrifuging, and then decantation of the liquid phase was conducted.

Specific radioactivity of products was measured under integral and differential regimes with a certificated instrumentation: in Progress-G gamma-spectrometer with a scintillation detection block and in PSO2-08 and DRG-01T radiometers. Processing of spectra, activity and error calculation were performed by means of the PROGRESS software package that was developed by VNIIFTRI and Doza Co. Exposure time amounted up to 1800 s depending on the activity of metered samples and their mass. The determination error was 11 % for the confidence probability of 0.95. The magnitude of β -radioactivity was determined in a low-background unit UMF-1500D.

RESULTS AND DISCUSSION

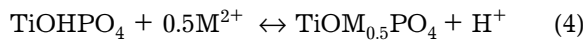
Capability of hydrated titanyl hydrophosphate to be involved in processes of cationic replacement is caused by the formation of a chelate bond between a bidentate ligand HPO_4^{2-} and a titanium (IV) ion. In response to a strong polarization of hydrophosphate ion in the field of the central atom, the mobility of the proton of the acidoligand is augmented considerably [13]. Meanwhile, hydrolysis of the sorbent is possible in aqueous mediums, with the result that a decrease of sorption properties occurs:



Results of investigations have demonstrated that sorbents on the basis of $\text{TiOHPO}_4 \cdot n\text{H}_2\text{O}$ are stable in acidic media. In the neutral medium, slow hydrolysis of sorbent is evidenced with its depletion by phosphate groups and with transformation of part of titanyl hydrophosphate into titanium oxohydroxide. The hydrolysis degree β of TiOHPO_4 in water at 20 °C does not exceed 2.25–2.70 % and decreases with an increase in the concentration of chlorides of alkaline elements in solutions, amounting, for example, to 1.7 % with $C_{\text{NaCl}} = 1$ mol/l. Replacement of a cation of alkali metal with a heavier one in the succession $\text{Na}^+ - \text{K}^+ - \text{Cs}^+$, as well as a decrease in the ratio of phosphorus and titanium in the sorbent causes hydrolytic stability of the solid phase to increase.

Sorption of cations of alkaline and alkaline-earth elements by amorphous titanyl

hydrophosphate $\text{TiOHPO}_4 \cdot n\text{H}_2\text{O}$ can be described by reactions



Exchange constants K_{exch} of metal cations to hydrogen ions by the reactions (3) and (4) are controlled by the respective ratios:

$$K_{\text{exch}} = N_{\text{M}}a_{\text{H}^+}/N_{\text{H}}a_{\text{M}^+} \quad (5)$$

$$K_{\text{exch}} = N_{\text{M}}a_{\text{H}^+}/N_{\text{H}}^{1/2}a_{\text{M}^{2+}}^{1/2} \quad (6)$$

where N_{M} and N_{H} are mole fractions of the protons of hydrophosphate groups that are replaced and not replaced by metal in the solid phase respectively; a_{H^+} , a_{M^+} and $a_{\text{M}^{2+}}^{1/2}$ are ionic activities of hydrogen and cations of alkaline and alkaline-earth metal in the solution, respectively.

From the values of thermodynamic constants K_{exch} of the reactions (3) and (4) that are given in Table 1 for cations of heavy and light elements that have been determined by a potentiometric method it follows that the use of a sorbent on the basis of titanyl hydrophosphate makes it possible to extract radionuclides of cesium and strontium with the required selectivity from LRW with elevated salinity that matches the composition of sea water.

Study of the sorption kinetics has revealed that when a powdered sorbent is used, time to reach an equilibrium is not over 15 min. When granular sorbents are used, time to attain the equilibrium increases and depends on the coarseness of the granules.

As suggested by the reactions (3) and (4), the distribution coefficient $K_{\text{d}} = A\alpha/(100 - A)$ (A is the fraction of the sorbed radionuclides from the initial (%); α is the ratio of the mass of the sorbent to the solution volume at a particular stage, g/cm^3) must depend on the

TABLE 1

Values of thermodynamic constant K_{exch} for the reactions (3) and (4)

Cation	K_{exch}	Cation	K_{exch}
Li^+	$1.5 \cdot 10^{-4}$	Cs^+	$2.5 \cdot 10^{-2}$
Na^+	$7.2 \cdot 10^{-4}$	Mg^{2+}	$2.5 \cdot 10^{-4}$
K^+	$6.3 \cdot 10^{-3}$	Ca^{2+}	$7.6 \cdot 10^{-4}$
Rb^+	$9.5 \cdot 10^{-3}$	Sr^{2+}	$2.5 \cdot 10^{-3}$
		Ba^{2+}	$6.3 \cdot 10^{-3}$

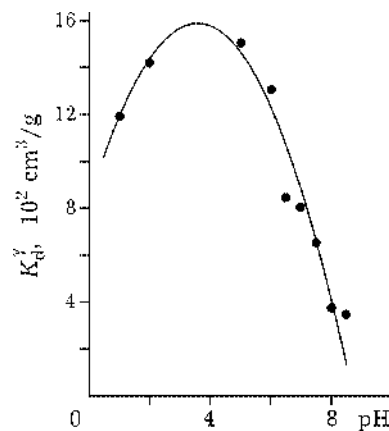


Fig. 1. Dependence of K_{d} for ^{137}Cs radionuclide on the suspension pH.

solution pH, which proves to be true in experiments during deactivation of real processing media (Fig. 1). A decrease of K_{d} at $\text{pH} < 2$ is related to the strengthening of the competition of hydrogen ions in a heterogeneous process of cation-exchange sorption on the solid phase, and at $\text{pH} > 6$, to the hydrolysis of titanyl hydrophosphate, and to its transformation in a less active form. Therefore, during the process of sorption of radionuclides from solutions with a high salinity, it is necessary to add an alkaline agent to maintain the optimum values of the pH that decreases because of the protons passing into solution [16].

Table 2 lists the K_{d} values for a powdered $\text{TiOHPO}_4 \cdot n\text{H}_2\text{O}$ containing 45–46.7 mass % of water (sorbent 1), and for a sorbent that represents titanyl hydrophosphate with the coarseness of the particles of 0.16 mm and the mass fraction of $\text{TiOHPO}_4 \cdot n\text{H}_2\text{O}$ being ~65 % that is uniformly distributed within the matrix of a hydrated silica (sorbent 2). During the determination of the K_{d} values, solutions with the following content of elements (in Bq/kg) were used as the initial ones: ^{134}Cs $1 \cdot 10^5$, ^{90}Sr $2.2 \cdot 10^4$, ^{60}Co $1 \cdot 10^4$. $\alpha = 60$ in the experiments. It is evident that the sorbent effectively absorbs all the main radionuclides that cause the radioactivity of LRW.

Sorption exchange capacity (SEC) of the samples was determined by the method of potentiometric titration in the solutions of chlorides of the appropriate metals at the concentration of electrolyte of 1 mol/l and pH 6. Table 3 gives the SEC values for certain alkaline and alkaline-earth cations, as well as for Co^{2+} cation.

TABLE 2

Distribution coefficient K_d of radionuclides for the sorbents 1 and 2, cm^3/g

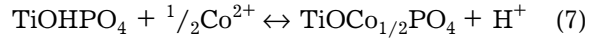
Radionuclide	Sorbent 1	Sorbent 2
^{134}Cs	1256	3080
^{90}Sr	1422	300
^{60}Co	332	128

TABLE 3

SEC data for the sorbents 1 and 2 at pH 6, mg-eq/g

Cation	Sorbent 1	Sorbent 2	Proportion of SEC for the sorbents 2 and 1
Na^+	2.96	1.93	0.652
Cs^+	3.37	2.14	0.635
Ca^{2+}	2.98	1.83	0.614
Sr^{2+}	3.17	2.08	0.656
Co^{2+}	1.89	1.52	0.804

The maximum, theoretically possible SEC of the sorbent 1 is 3.33–3.44 mg-eq/g . It is evident from Table 3 that the SEC of the sorbent 1 is no less than 85 % from the theoretically possible for light (Na^+ , Ca^{2+}) and 92–98 % for heavy (Cs^+ , Sr^{2+}) cations of alkaline and alkaline-earth elements. An appreciably smaller SEC value for cobalt appears to be related to the circumstance that cobalt salts are hydrolyzed at pH 6 with the formation of difficultly sorbed cations of a complicated composition. When pH is decreased down to 4.9, SEC of the sorbent 1 for Co^{2+} rises to 2.46 mg-eq/g , although an increase in the acidity of the solution must cause deterioration of the sorption by the reaction



For the majority of the studied cations, SEC of the sorbent 2 corresponded to its content of titanyl hydrophosphate. It is believed that hydrated silica, the carrier of titanyl hydrophosphate, is not perceptibly involved in the sorption of cations of alkaline and alkaline-earth elements.

For the granular sorbent with a coarseness of granules of 0.2–0.7 mm, the SEC has appeared to be just 7.6–11.6 % less as compared to the powdered sorbent, while for the sorbent with a coarseness of granules of 0.7–2.0 mm, it dropped down to the level that has been received for the sorbent 2. It is related to diffusive restraints when sorbed cations enter in depth of particles and when protons are released from the sorbent particles into the solution. Study of the sorbents that contain titanyl oxohydroxide along with titanyl hydrophosphate reveals a decrease in SEC (Table 4).

To increase the efficiency of the use of the sorbent, deactivation was conducted under a counter-flow regime (Fig. 2). The pH value that corresponds to the maximum magnitude of K_d was maintained by the injection of the appropriate amount of soda.

The number of stages N was found from the required purification degree from radionuclides based on γ - and β -activity according to the ratio

$$N = (\ln A_{\text{init}} - \ln A_{\text{fin}}) / (\ln K_d + \ln \alpha) \quad (8)$$

where A_{init} and A_{fin} are specific γ - or β -activity in the initial and final solutions respectively; K_d is the distribution coefficient of radionuclides over the respective γ - or β -activity.

TABLE 4

SEC data for sorbents of various compositions at pH 6, mmol/g

Sample	Chemical composition	Cation	SEC
1	$\text{TiOHPO}_4 \cdot 2.15\text{TiO}(\text{OH})_2 \cdot 3.15\text{H}_2\text{O}$	Na^+	2.16
		Cs^+	2.33
2	$\text{TiOHPO}_4 \cdot 0.84\text{TiO}(\text{OH})_2 \cdot 2.35\text{H}_2\text{O}$	Na^+	2.68
		Cs^+	3.02
3	$\text{TiOHPO}_4 \cdot 0.12\text{TiO}(\text{OH})_2 \cdot 2.13\text{H}_2\text{O}$	Na^+	3.10
		Cs^+	3.49
4	$\text{TiOHPO}_4 \cdot 3.17\text{H}_2\text{O}$	Na^+	3.20
		Cs^+	3.69

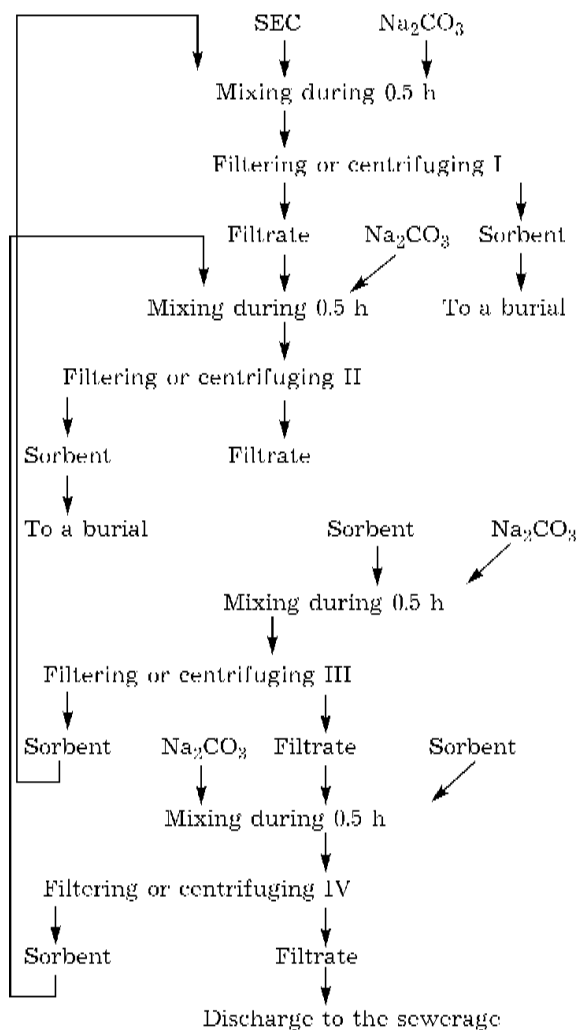


Fig. 2. Flow chart for LRW with an elevated (32 mg/l) salt background that corresponds to sea water in its composition that is purified by amorphous sorbent.

Deactivation of LRW was performed to meet sanitary regulations. The content of petroleum derivatives of the cleared solution was equal to <0.1 mg/l, which is less than the standard that is specified for fishery water bodies. Under optimum conditions, the equilibrium specific radioactivity of the solid phase was as large as $\approx 1 \cdot 10^7$ Bq/kg.

Thus, the investigations have made it possible to recommend amorphous sorbents based on $\text{TiOHPO}_{4x} \cdot n\text{H}_2\text{O}$ for application in the decontamination of LRW with the higher than usual salt background that additionally contain impurities in the form of petroleum derivatives and solid suspensions. The latter have no considerable effect on the deactivation of liquid wastes and they can be separated from the solution being cleared together with the waste sorbent.

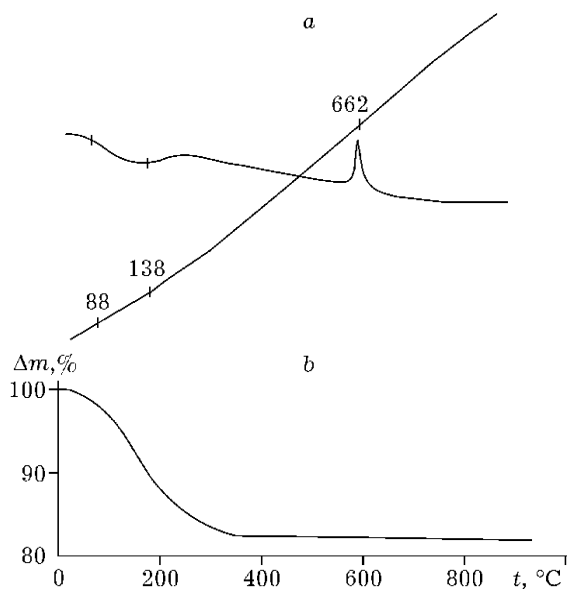


Fig. 3. Curves of DTA (a) and TG (b) analysis of the waste sorbent.

The sorbent that is saturated by radionuclides represents the hydrated product that is again capable of eliminating radionuclides during its storage in a humid atmosphere. Therefore, it is advisable to conduct its thermal treatment before its burial and this treatment is accompanied by an endothermic effect that corresponds to elimination of the adsorptive and coordination water at a temperature of less than 200°C (Fig. 3, a, b). Further heating of the samples is followed by an exothermal effect of crystallization.

The investigations of hydrolytic stability of the samples of a calcinated waste sorbent have demonstrated that it is not subject to hydrolysis upon holding for 8 months in an aqueous slurry (pH 4–8). No desorption of radionuclides into the aqueous phase is observed. It is believed that the burial of the waste sorbent after its thermal treatment can be realized by concreting, bituminization or vitrification. By virtue of the fact that the content of chemically bounded water in the initial sorbent can amount up to 46.7%, the mass of the sorbent entering to a burial place considerably decreases owing to water-removal during the thermal treatment.

The performed investigations allow a conclusion on the viability of the application of sorbents based on titanyl hydrophosphate in the development of the process to rehabilitate certain polluted territories. The authors [17] have

found that more than 97.8 % of radionuclides that are kept for the most part by cambrian clay were leached into a solution by nitric acid for a single stage from the polluted soil of the 5th quarter of the Vasilievskiy Island (St. Petersburg). Therefore, we have approved certain basic decisions that involve transfer of radionuclides from polluted soils into a solution by acid-salt treatment (by solutions of nitric acid and sodium nitrate) with the subsequent neutralization of the radioactive solution by soda and with sorption of radionuclides from it by sorbents on the basis of titanyl hydrophosphate. Then the deactivated solution of sodium nitrate was acidified and recycled to leaching of radionuclides from the following batch of soils. An immobilization of radionuclides in a saturated waste sorbent was conducted through heat treatment. The deactivated solution on the basis of sodium nitrate can be also processed by electro dialysis to yield nitric acid and sodium hydroxide that are then recycled into the process. Electro dialysis processing of solutions of nitrates of alkaline elements has been developed on a trial scale [18]. Preliminary results have confirmed the possibility in principle for deactivation of podsollic soils under the above approach. However, it should be remarked that the development of the process to rehabilitate polluted territory must include optimisation of all operations with allowance for the features of radionuclide transfer into solution, and these features are controlled by a peculiar mineralogical composition of soil in each specific case.

CONCLUSIONS

Sorbents on the basis of titanyl hydrophosphate are complex, since they provide simultaneous clearing LRW from disintegration products of nuclear fuel, namely, caesium, strontium, and cobalt radionuclides.

A distinctive feature of the mentioned sorbents is their high selectivity for sorption of heavy

cations on the background of a great excess (at least, 1 mol/l) of competing light cations, both from chloride, and from nitrate media.

Sorbents on the basis of titanyl hydrophosphate can be produced in a powdered or granular form, which admits carrying out the deactivation of LRW both with the use of chemical reactors, and sorption columns.

A set of properties of the sorbents on the basis of titanyl hydrophosphate determines their viability for the development of highly effective technology for rehabilitation of certain polluted territories that includes sorption of radionuclides from salt liquors.

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