

Development of a purification technology for treatment of medium- and low-activity radioactive waste of radiochemical production from Co-60 and Cs-137

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Abstract. The technological flowchart of purification of medium- and low-activity waste from Co-60 and Cs-137 is developed and introduced. The developed purification scheme has been successfully tested using genuine medium- and low-level liquid radioactive waste of radiochemical production containing complexing and colloid forming components (complexons, surfactants). The optimal conditions of the presented method of purification ensure reduction of the residual specific activity of ⁶⁰Co and ¹³⁷Cs radionuclides in the solution to less than 0,9 Bq per litre.

1 Introduction

A critical task for providing radiation safety at radiochemical plants is solution to the problem of treatment and reprocessing of liquid radioactive waste (LRW), generated from the operation of power installations, various technological procedures with solutions containing radionuclides, during decontamination of equipment, etc. Liquid radioactive wastes are collections of wastes from drains collectors and vacuum drainage of floor, decantates from clarifiers, liquid wastes from specialized laundries. In case of considerable volumes of LRW not only decontamination factor (index), but also residue levels of radionuclides in solutions after their treatment are critical, that enables reuse of water resources without boiling and utilization of stillage residue. The main radionuclides which LRW are purified from are ¹³⁷Cs, ⁶⁰Co. Ion-selective methods of purification from ⁶⁰Co used in the technology suggests preliminary acid treatment of solutions aimed at destroying complexing agents and subsequent stages of radionuclide release, e.g., use of inorganic sorbent agents and cation exchange resins used for desalinization. The employed methods ensure efficient decontamination from ¹³⁷Cs with decontamination factor of $10^2 \div 10^4$. However, the decontamination factor for ⁶⁰Co is usually less than 102, which does not allow reducing general activity of solutions after treatment of less than $10 \div 50$ Bq/L.

The process solutions of LRW, generally, contain not only such components fed into solutions as aminopolycarboxylic acids; ethane diacid, citric acid, tartaric acid and their salts; sodium salts of ethylenediaminetetraacetic (EDTA) and diethylene triamine pentaacetic acids (DTPA), but also organic components with variable composition, formed as a result of radiolysis on long storage of LRW which form with ⁶⁰Co complex chelated compounds with high stability constants [1,2]. Therefore, a prerequisite for increasing decontamination factor for ⁶⁰Co is total destruction (oxidation) of all organic components of LRW regardless of their composition. Surfactants contained in the solutions (anionic, ampholytic, and nonionic SAS), high-molecular compounds, biocolloids also require both techniques intensifying oxidation decomposition and methods for special destruction of a colloid, containing ⁶⁰Co.

Well-known methods of extracting the radionuclide ⁶⁰Co from LRW at nuclear power plants are introducing Fe (III) and Ni (II) cations into LRW upon contact with potassium ferricyanide with molecular ratio from 2:1 to 4:1, allowing the solution to stand at room temperature and centrifugal separation of residue [3]. However, since there is no stage of oxidation of organic components of LRW, reagent consumption and sludge formation increase. Moreover, the technological adaptation of these methods requires expensive equipment, necessary for removing fine-grained sludge – a cascade of filtering centrifuges with the separation factor not less than 15000.

Treatment of LRW generated at nuclear power stations involves their preliminary vaporization resulting in formation of condensate and stillage residue, ozonation of stillage residue, removal of radioactive slurry and concentrating the filtrate by deep evaporation [4,5]. The main drawbacks of this method are: insufficiently effectiveness of a special stage

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of ^{60}Co extraction from the solution after ozonation and, as a result, inefficient removal of ^{60}Co , that requires concentrating the filtrate by evaporation; high power consumption of the process; increased reagent consumption (ozone); need to keep constant pH level; as well as exclusive fire- and explosion safety requirements during the process. LRW stillage residue is also purified from radioactive cobalt and cesium by oxidation of stillage residue with hard ultra-violet rays (UV) and removal of corrosion products by filtration [6,7]. We must also note low efficiency and technological complexity of arranging LRW oxidation in dynamic regime, technological complexity of arranging LRW oxidation in the static regime due to the process time (over 6 hours), reduced efficiency of UV-lamp when the salt content is over 10 g/l and increased turbidity leading to inefficient oxidative destruction of organic components of LRW and removal of radionuclides.

2 Experimental

The aim of the research is to develop a technologically applicable method for purification of medium- (MAW) and low-activity waste (LAW) from ^{60}Co with simultaneous purification from ^{137}Cs at radiochemical plants. The task was to reduce remaining specific activity of MAW and LAW solutions in terms of ^{137}Cs and ^{60}Co content to the level, sufficient to classify LRW as non-radioactive waste according to the requirements of OSPORB-99/2010 [8] (allowing subsequent use of purified solutions).

A comprehensive approach aimed at increasing the decontamination index of medium- (MAW) and low-activity (LAW) LRW from ^{60}Co , ^{137}Cs and ensuring the required level of radionuclides removal involves catalytic oxidation of organic components of LRW and coagulative and precipitative extraction of radionuclides with mixed ferricyanides of transition metals followed by subsequent treatment of filtrate with cation exchange resin. The technological flow-chart of the developed method of purification is given in figure 1. The critical factor is the adequacy of destruction of complexing and colloid forming (organic) agents of LRW.

As stock solution for purification genuine slurry decantates after precipitation of drainage and desorbing solutions, formed after decontamination of production equipment at the spent fuel storehouse WWER-1000 and equipment in the independent spent-fuel storage installation room RBMK-1000 were used. The composition of stock solution (used during the research) is given in Table 1.

Table 1. Chemical and radionuclide composition of stock solution.

Component or criteria	Dimension	Value
Total salt content	g/l	20÷70
Oxalate-ion	g/l	2
Carbonate-ion	g/l	2
EDTA	mg/l	0÷100
ASs (anionic surfactants)	mg/l	1,5÷50
pH		8,9÷9,2
Cs^{137}	Bq/L	up to $4,56 \times 10^4$
Co^{60}	Bq/L	up to $1,02 \times 10^3$

Well-known catalysts for oxidation destruction of organic compounds in nitric acid media are platinum catalysts, applied to anion exchange resins (VP-1AP and other), silica gels, carbons, etc. [9-11]. Despite the advantages of heterogeneous catalytic processes, their industrial application in radiochemical technology is limited, firstly, due to the high cost of the (platinum) catalyst and non-recoverable losses of a platinum-group metal in the course of operation. As solid state catalyst of oxidation destruction of organic components of LRW in nitric acid media we use: platinum catalyst (Pt/VP-1AP), applied to anion exchange resin VP-1AP (GOST 20301-74) with platinum weight content of up to 2%, and two new types of solid state catalysts developed by the authors – nickel-ferricyanide catalyst [12] on VP-1AP carrier and bimetal platinum-zirconia catalysts (carriers – silica gel, aluminum oxide) [13].

Characteristics of the prepared solid state catalysts used during the process are given in Table 2. Total surface area of catalysts is determined using the method of thermal desorption of nitrogen. Chemical activation of the obtained catalysts is carried out in the dynamic regime with 20÷55 column volumes of 1,5 mol/L solution of nitric acid at the speed of 7÷12 column volume per hour.

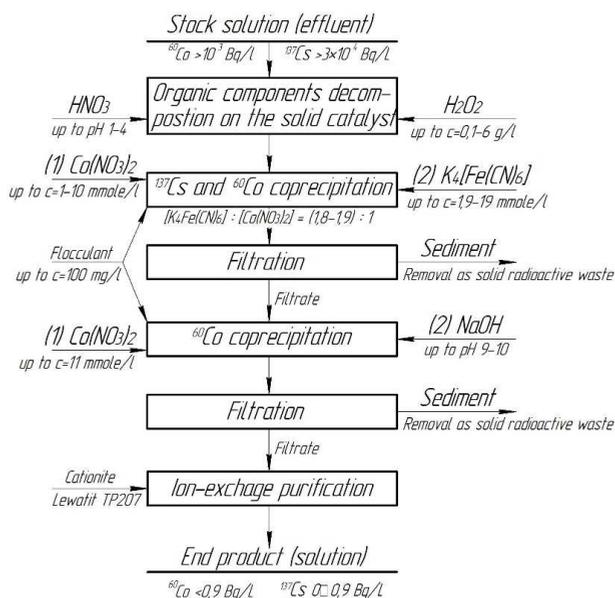


Fig. 1. Flowchart of purification of medium- and low-activity waste from ^{137}Cs and ^{60}Co .

Table 2. Characteristics of the catalysts used during the research.

Catalyst	Catalyst carrier	Pt, %	Particle size distribution, mm	Surface area, m ² /g
Pt / VP-1AP	Anion exchange resin	1,97	0,3 ÷ 0,5	18,47
Pt / Zr / SiO ₂ (Al ₂ O ₃)	Silica gel (Aluminum oxide)	0,08	0,25 ÷ 0,35	70,31 (10,47)
R-Ni[Fe(CN) ₆]	Anion exchange resin	-	0,3 ÷ 0,5	18,36

Testing of regimes and optimization of the developed method of purification of MAW and LAW from radionuclides ^{60}Co and ^{137}Cs is assessed on the results of experiments (research) on the laboratory installation given in Fig. 2.

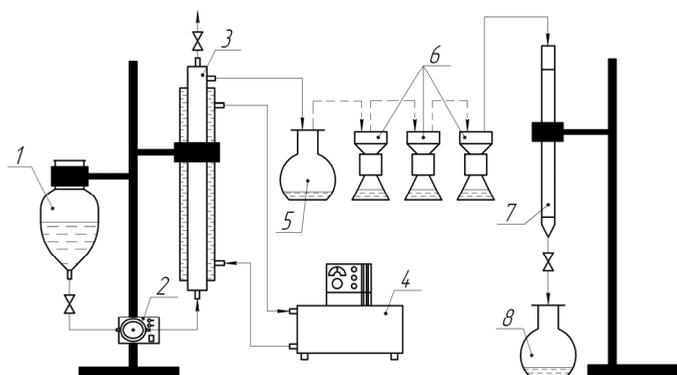


Fig. 2. Laboratory installation diagram of LRW purification from ^{60}Co and ^{137}Cs .

Laboratory installation includes: a stock bottle with stock solution (1), a peristaltic pump (2), a catalytic oxidation column (3), a thermostat (4), a stock bottle for receiving solution from the catalytic column (5), receiving filters with removable fluoroplastic cartridges (6), an ion-exchange column (7), a receiver stock bottle for purified solution (8).

LRW is purified in the following sequence: the LRW solution to be treated, regardless of its conditions, is corrected with hydrogen nitrate up to pH 1÷4. Next, hydrogen peroxide is added to reach concentration of hydrogen peroxide in the solution of up to 0,1-3,3 g/L. The corrected solution passes through the first stage of LRW purification in the catalytic oxidation column, operating at 47,5÷80°C, having the flow speed of 3÷15 column volume/per hour, that ensures contact time of the solution with the catalyst in the interval of 50÷130 sec.

The developed method and catalytic oxidation mode ensure 99,85-99,91 % of decomposition of organic components of LRW (EDTA, oxalate-ion, ASs), which can be achieved when using the indicated types of solid state catalysts, given in Table 2, and depends on the concentration of an organic component in the stock solution. The residual value of organic components does not exceed 100 µg/l.

The laboratory catalytic column is a device made from quartz glass with bottom feed of solution, a laminar flow zone, a catalysis zone, a gas separation zone. The catalysis zone is divided by meshed partitions. The prepared catalyst is loaded through the upper gate and squeezed by the upper meshed partition. In this case, the pore volume of the catalyst granular bed is 5,1÷12,5% of the bulk volume. The catalyst zone is a vertical cylindrical column filled with catalyst with «diameter/height» ratio of 1:3÷1:15. The catalyst is a uniformly graded inorganic porous carrier, silica gel or anion exchange resin with the grain size of 0,25÷0,50 mm, an active surface area of 18÷71 m²/g with a layer of ultrafine homogeneous chemically inactive in weak solutions of nitric acid metal (salt) composition with ratio to the carrier of 0,08-7,5% mass, which are both oxidation catalysts of organic components of LRW and decomposition catalysts of hydrogen peroxide followed by formation of a hydroxyl radical.

The solution which has gone through the phase of catalytic oxidative destruction proceeds to the second stage – flocculation and precipitation. At the first operation a transition metal nitrate (Co, Ni, Zn) is added to the solution up to a concentration of 1,0-12,6 mmol/L. Then, while stirring intensively for 15÷20 minutes, solution of Besfloc K-051C flocculant is added up to a concentration of 10-100 mg/l, followed by addition of solution of an alkali metal ferricyanide up to a concentration of 1,9-19,0 mmol/L. In this case, the molecular ration between a transition metal nitrate (Co, Ni, Zn) and an alkali metal ferricyanide is from 1,0:1,5 to 1,0:1,9. Upon the total sedimentation of residue after 0,5÷2,2 hours the clarified part is decanted, i.e. intermediate filtration is carried out at the speed of 5,0-15,0 mL/min·cm² through MFFK-3G membrane (0,45µm pore size), MFFK-4G (0,65µm pore size) or TRUMEM membrane with 0,45-0,60 µm pore size. Dense precipitate from the reactor bottom is deposited on the removable cartridge of the receiving filter and filtrated at the speed of 0,2÷7,0 mL/min·cm² through MFFK-1G membrane (0,15µm pore size), MFFK-2G (0,25µm pore size) or TRUMEM membrane with 0,15÷0,25µm pore size. Decantate and filtrate are combined and proceed to the next operation of the flocculation and precipitation stage.

Here, Besfloc K-051C flocculate is added, while being stirred intensively, to the solution which has a residual concentration of alkali metal ferricyanide of 0,9-6,4 mmol/L up to a concentration of 10-100 mg/l. Then, diethyldithiocarbamate of an alkali metal is added up to a concentration of 10-100 mg/l. Further, the solution is mixed during 10-15 minutes and a transition metal nitrate (Co, Ni, Zn) is added up to a concentration of 1,8-12,8 mmol/L. It ensures excess of a transition metal nitrate (Co, Ni, Zn) as compared to ferricyanide. At the second operation precipitate detachment is similar to one at the first operation. The obtained decantate and filtrate are combined and proceed to the third operation of the flocculation and precipitation stage.

Then, Besfloc K-4000 flocculate is added, while being stirred intensively, to the solution up to a concentration of 10-100 mg/l, followed by addition of sodium hydrate solution up to pH 9-10. At the third operation precipitate detachment is similar to one at the first operation. The second and the third operations can be combined without intermediate detachment of sediment. All three operations can also run subsequently in one device if to use an intermediate container for filtrates and decantates.

Final purification from ⁶⁰Co is carried out with cation exchange resin, selective to ions of transition and heavy metals, e.g., Lewatit MonoPlus TP 207, which is a weakly basic macroporous cation exchange resin with chelate groups of iminodiacetic acid. The solution passes through the ion-exchange column at the speed of 4÷10 column volume/per hour, with «diameter/height» ratio of the filling layer geometry of 1:10÷1:20. The third stage – ion-exchanging – can be excluded, in case the salt content of filtrate after coagulation and precipitation stage does not exceed 10 g/l.

3 Results and discussion

The developed method has significant advantages over the known (indicated earlier [3]-[7]) methods of purification of LRW generated at radiochemical plants and nuclear power stations due to a more complete oxidation of organic components of LRW in the dynamic mode of the column operation during considerably less time available for contact (50÷130 sec) combined with high efficiency of the column (3÷15 column volume/per hour), at lower temperature of the process (47,5÷80°C). A column with the filling layer of a catalyst and a dynamic mode of oxidation decomposition stage condition simple hardware arrangement of the process. Process variables do not depend on turbidity and salt composition of the solution and allow a wide range of the flow rate and temperature setting without sacrificing oxidation efficiency of organic components of LRW, which enables treatment of cloudy solutions (e.g., decantates) without preliminary clarification. Process variables (contact time, efficiency) can be easily changed in terms of both increase/decrease of the height of the catalyst filling layer and flow rate. Application of a catalytic mechanism of oxidation decomposition allows significantly reducing the amount of hydrogen peroxide added to LRW up to 3% volume (unlike UV-treatment of stillage residue) at the oxidation stage. Oxidation decomposition is carried out in acidic medium at pH 1÷4, which allows taking an advantage of synergism resulting from addition of low concentration of the second oxidizing agent – hydrogen nitrate during catalyst oxidation. The solution is mixed in the contact zone due to intensive spontaneous gas release in the pore space of the catalyst filling layer that increases the flow turbulence and decreases the contact time. The suggested method

excludes sludge formation and precipitation of products of oxidation decomposition at the stage of oxidation decomposition. Thus, extraction of solid phase prior to coagulation and precipitation can be neglected.

An alkali metal diethyldithiocarbamate is added at the second operation of the coagulation and precipitation stage (when the base quantity of ^{60}Co (65,1÷95,4%) has already precipitated with mixed ferricyanides). It is added into dilute acidic solution (pH 1÷4), containing ferricyanide of an alkali metal and flocculant, which ensures precipitation of ^{60}Co in ion form (the most suitable for fixation of cobalt with diethyldithiocarbamate). The sequence of addition of an alkali metal diethyldithiocarbamate allows, unlike the method described in [4], initial binding of radioactive cobalt with diethyldithiocarbamate (resulting in formation of finely dispersed flocculated cloud, detected by turbidity change of the LRW solution). After 10-15 minutes of contact a transition metal nitrate (Co, Ni, Zn) can be added followed by coprecipitation of ^{60}Co , remaining in the solution, both with residue of a transition metal diethyldithiocarbamate (Co, Ni, Zn) and with residue of a transition metal ferricyanide (Co, Ni, Zn). Since an excessive amount of transition metal nitrate (Co, Ni, Zn) is used, the whole diethyldithiocarbamate is removed from the LRW solution with a precipitate, without polluting LRW with the added organic components. In case of simultaneous coprecipitation of diethyldithiocarbamate of a transition metal (Co, Ni, Zn) and ferricyanide of a transition metal (Co, Ni, Zn) dense precipitate is formed which is easily removed by microfiltration. The suggested method ensures reducing the amount of the introduced diethyldithiocarbamate of an alkali metal more than 100 times, when using it in concentration of 10-100 mg/l (considerably lower as compared to [6]).

When analyzing the results of the experiments conducted on the laboratory installation and improvement of the method of LRW (MAW, LAW) purification from radionuclides, efficiency of the developed method was estimated. The data are given in Table 3.

Table 3. Estimate of efficiency of the developed method of purification from ^{60}Co and Cs^{137} .

№ of treatment stage	Solution activity after treatment, Bq/L		Decontamination index	
	Co^{60}	Cs^{137}	Co^{60}	Cs^{137}
<u>I stage:</u> Catalytic oxidation of the solution	$1,02 \times 10^3$	$4,56 \times 10^4$	-	-
<u>II stage:</u> Coprecipitation of ^{60}Co and ^{137}Cs radionuclides with mixed ferricyanides of transient metals (Co, Ni, Zn)	6	16	170	2850
Coprecipitation of ^{60}Co with Na-diethyldithiocarbamate mixed with ferricyanides of transient metals (Co, Ni, Zn)	3,5	5	1,72	3,20
Coprecipitation of ^{60}Co with hydroxides of transient metals (Co, Ni, Zn)	2	3,6	1,75	1,39
<u>III stage:</u> Ion-exchange purification	< 0,9	< 0,9	> 2,20	> 4
Result			> 1133	> 51667

Low decontamination indexes during after-purification stages are conditioned by low content of radionuclides in the solution (after the first operation of coprecipitation) versus content of an added stable transition metal. The aim of the final ion-exchanging purification in the developed scheme is a barrier protection from slip of removed cobalt-60 radionuclides. At this stage it is important not to ensure high decontamination indexes, but a stable maximum low content of both radionuclides in the flowing solution and added salts of transient metals.

After extracting ^{60}Co and ^{137}Cs radionuclides (with activity lower than 0,9 Bq/L), the solutions, according to [8], do not belong to radioactive waste and do not require any measures on reducing radioactivity which allows their later use for different technological operations.

As a result of a successful laboratory testing of the developed method a technological flowchart for purification of MAW and LAW from ^{60}Co and ^{137}Cs (see fig 3) was suggested. The installation includes: a stock bottle with stock solution of LRW (1), membrane pumps (2,6,9,12,15), a catalytic oxidation column [14] (3), a thermostat (4), a stock bottle for receiving solution from the catalytic column (5), «mixer tank-settling tank» reactors (for every operation of coagulation and precipitation stage, and which have sedimentary residue zones and decantate removal zones) equipped with an agitator (7,10,13), receiving filters with remotely-removable fluoroplastic cartridges (8,11,14), ion-exchanging column (16), control valves (B01÷B33).

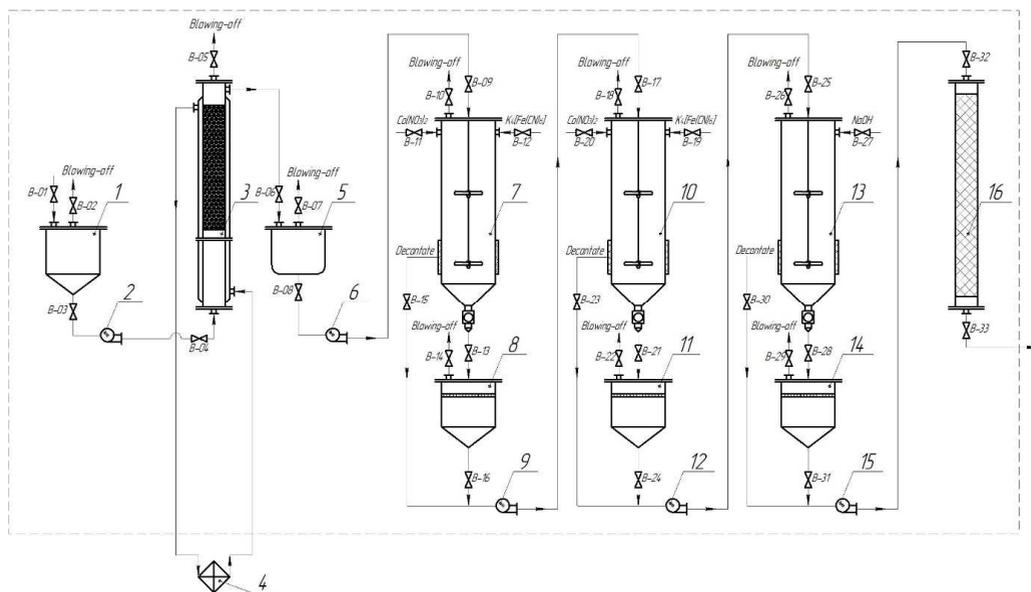


Fig. 3. Technological flowchart of the purification process of medium- and low-activity waste from ^{60}Co and ^{137}Cs .

4 Conclusions

The developed process of LRW purification from ^{60}Co and ^{137}Cs has been successfully tested using real medium- and low-level liquid radioactive waste of radiochemical production containing complexing and colloid forming components (complexons, SAS).

The optimized parameters of the process of purification allowed reducing residual specific activity of ^{60}Co and ^{137}Cs in the solution up to less than 0,9 Bq/L.

A technological flowchart for purification of MAW and LAW from ^{60}Co and ^{137}Cs was developed and suggested for application.

The analysis of the results allows considering the developed method to be technologically applicable for treatment of decontamination fluids, drain water, wastes from specialized laundries at radiochemical enterprises, containing different concentrations of complexons and SAS.

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