

Article

Toward Deep Decontamination of Intermediate-Level-Activity Spent Ion-Exchange Resins Containing Poorly Soluble Inorganic Deposits

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Abstract: Spent ion-exchange resins (SIERs) generated yearly in large volumes in nuclear power plants (NPPs) require particular predisposal handling and treatment with the primary objectives of waste volume reduction and lowering the disposal class. Deep decontamination of the SIERs using solution chemistry is a promising approach to reduce the amount of intermediate-level radioactive waste (ILW) and, thus, SIER disposal costs. However, the entrapment of nonexchangeable radionuclides in poorly soluble inorganic deposits on SIERs significantly complicates the implementation of this approach. In this work, the elemental and radiochemical compositions of inorganic deposits in an intermediate-level-activity SIER sample with an activity of 310 kBq/g have been analyzed, and a feasibility study of SIER decontamination using solution chemistry has been conducted. The suggested approach included the magnetic separation of crud, removal of cesium radionuclides using alkaline solutions in the presence of magnetic resorcinol-formaldehyde resin, removal of cobalt radionuclides using acidic EDTA-containing solutions, and hydrothermal oxidation of EDTA-containing liquid wastes with immobilization of radionuclides in poorly soluble oxides. The decontamination factors for ¹³⁷Cs, ⁶⁰Co, and ⁹⁴Nb radionuclides were 3.9×10^3 , 7.6×10^2 , and 1.3×10^2 , respectively, whereas the activity of the decontaminated SIER was 17 Bq/g, which allows us to classify it as very low-level waste.

Keywords: spent ion-exchange resins; resorcinol-formaldehyde resins; radionuclides; activated corrosion products; decontaminating solutions; EDTA; hydrothermal oxidation



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1. Introduction

Radioactively contaminated spent ion-exchange resins (SIERs) are a specific type of radioactive waste generated at various stages of the nuclear power cycle. In nuclear power plants (NPPs), SIERs are accumulated as a result of the operation of a cleanup system for the primary coolant, decontamination of water from cooling ponds, deactivation solutions, trap water, and water streams from special water decontamination systems. The total volume of SIERs generated in NPPs is estimated as 0.02–0.025 m³/MW of nominal power for two-circuit reactors of WWER-type NPPs and 0.08–0.025 m³/MW of nominal power for single-circuit reactors of RBMK-type NPPs [1].

SIERs, which accumulate radionuclides and chemical impurities and cannot be re-generated and reused, are present in the form of low-level radioactive waste (LLW) and intermediate-level radioactive waste (ILW) and have to be conditioned to meet the waste acceptance criteria for a disposal site. The primary objectives of SIER management are based on the IAEA Technical Document for Management of Spent Ion-Exchange Resins from Nuclear Power Plants [2] and include volume reduction, immobilization, storage, disposal, and economic issues. Currently, applied SIER conditioning methods include

direct solidification using inorganic and organic compounds (cement, bitumen, and plastics) [3–6] and the destruction of the organic matrix via combustion, pyrolysis, liquid phase oxidation, supercritical water oxidation, or plasma combustion [7–10]. While destructive methods allow a significant reduction in the volume of solid radioactive wastes to be sent for disposal, this approach is complicated by the high-temperature release of gaseous destruction products and the demand for expensive corrosion-resistant equipment. The direct solidification of SIERs is the first-choice option in many cases, but it leads, as a rule, to an increase in waste volume. Considering the high difference in disposal costs between LLW and ILW, blending or concentration averaging intermediate- and low-activity SIERs was shown to be an efficient way to reduce the amount of waste stored, lower the disposal class, and minimize disposal costs [11,12].

From our point of view, a very promising approach to safe and economically sound SIER management is based on the deep decontamination of resins using specially selected solutions. This will enable one to lower SIERs' disposal class or, in the ideal case, to reach a level meeting criteria for industrial (nonradioactive) solid waste. Spent deactivation solutions containing radionuclides can be processed with the common methods used for conditioning liquid radioactive wastes (LRWs) to assure safe radionuclide immobilization. The deep decontamination approach has been previously tested on low-level-activity SIERs at the Balakovo and Kalinin NPPs (Russia). The decontamination scheme included the treatment of SIERs with highly acidic solutions with subsequent immobilization of cesium radionuclides on selective ferrocyanide sorbents. The specific activity of SIERs was reduced to the level of nonradioactive wastes [13], which demonstrated the applicability of the proposed strategy to the reduction in radioactive waste volume without the destruction of the SIER matrix. However, despite the obvious advantages of this approach, it has been scarcely investigated and reported in the literature so far.

One of the problems in SIER decontamination using a deactivation solution is the presence of poorly soluble inorganic deposits. Such deposits can be formed during the purification of the coolant and condensate (crud removed from the nuclear reactor core) and the processing of SIERs from the intermediate storage together with inorganic filter materials (for example, perlite) [14,15]. Moreover, the deposition of the dissolved impurities on resins used in water purification systems is also possible during operation. In this case, different types of deposits can be formed depending on the pH and water composition, which is rather typical for mixed-bed ion-exchange filters. For example, the hydrolysis of dissolved iron ions leads to the precipitation of iron hydroxides [16,17], which is accompanied by the coprecipitation of corrosion radionuclides (e.g., ^{60}Co) and a subsequent formation of the mixed oxide phase. Since many of such oxides are insoluble in nitric acid, which is used for the regeneration of ion-exchange resins, they are accumulated in resins from cycle to cycle. The radionuclides occluded by oxide particles are also accumulated. The presence of Si and Al in the water streams, as a rule, leads to the formation of polysilicic and aluminum-polysilicic acids and their subsequent transformation to poorly soluble aluminosilicate deposits both on the surface and inside of ion-exchanger beads [18–20]. A characteristic feature of such deposits consists of the ability to capture cesium ions at the stage of deposit formation and after via adsorption. Despite a strict restriction on the Si content in NPP waters, it continuously enters the circuit and other water streams from the following potential sources: corrosion of stainless steels (containing up to 1% Si); suction of technical water from coolers through leaks in pipe fittings; perlite from precoat filters; defoamers used in evaporation system (bentonite clay and organosilicon compounds); and technical water from special laundry and sanitary facilities [14,15,21,22].

The binding of radionuclides by the insoluble deposits significantly reduces the efficiency of SIER decontamination by acid–base regeneration. Thus, high decontamination factors for SIERs can be achieved only via the removal of non-ion-exchangeable radionuclides.

We have shown earlier that cesium radionuclides can be removed from resins contaminated with silicate deposits using alkaline deactivation solutions (DSs). This approach was applied for the decontamination of a low-level-activity SIER sample from the re-

search reactor in a scheme including a transfer of the released cesium radionuclides to resorcinol-formaldehyde resins and then to a ferrocyanide sorbent [23].

In the present work, further development of the earlier proposed scheme and its application to the decontamination of an intermediate-level-activity SIER sample from the storage facility of Units 1 and 2 of the Kursk NPP with ^{137}Cs activity of 10^7 Bq/kg are reported. This task was additionally complicated by the presence of iron oxides and corrosion radionuclides with ^{60}Co activity above 10^6 Bq/kg in the SIER sample.

2. Materials and Methods

2.1. Materials

2.1.1. Reagents

All the reagents used in the present work (sodium nitrate NaNO_3 , sodium hydroxide NaOH , disodium ethylenediaminetetraacetate dihydrate $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$, zinc nitrate hexahydrate $\text{ZnNO}_3\cdot 6\text{H}_2\text{O}$, resorcinol $\text{C}_6\text{H}_4(\text{OH})_2$, formaldehyde CH_2O , iron(III) chloride $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$, iron(II) sulfate $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, nitric acid HNO_3 , ammonium hydroxide NH_4OH , and hydrogen peroxide H_2O_2) of a chemically pure grade were purchased from NevaReaktiv LLC (St. Petersburg, Russia) and used without further purification. Siloxane-acrylate emulsion (KE 13–36), with a particle size of 160 nm and solid phase content of 50%, was produced by the scientific production association “Astrokhim” (Elektrostal’, Russia).

2.1.2. Spent Ion-Exchange Resin (SIER)

SIER was sampled from the temporary storage tanks of Units 1 and 2 of Kursk NPP with an RBMK-1000 reactor (high-power channel reactor). Samples were taken using a cylindrical sampler at 1/2 of the depth from the surface of the tank and placed into clean plastic containers for characterization. The SIER sample was a polydispersed mixture consisting of brown spherical resin beads (cationite KU-2 and anionite AV-17) and fine dark-brown powder. The radionuclide composition of the sample was determined as described in Section 2.7.

2.1.3. Ferrocyanide Sorbents

Termoksid-35, a spherically granulated sorbent based on nickel-potassium ferrocyanide (32–36 wt %) immobilized in the pores of highly dispersed amorphous zirconium hydroxide, produced under Technical Conditions 6200-305-12342266–98, was purchased from Termoksid Ltd., Zarechny, Sverdlovsk Region, Russia, and used as a 0.25–0.5 mm fraction with a bulk density of 1.3 g/cm^3 .

FNK-50, nickel-potassium ferrocyanide (50 wt %) coprecipitated with silicic acid gel, was purchased from JSK “Alliance Gamma”, Russia, and used as a 0.2–0.25 mm fraction with a bulk density of 0.6 g/cm^3 .

2.1.4. Synthesis of Resorcinol-Formaldehyde Resin (RFR) and Iron Oxides

Magnetic composite sorbent RFR-M was synthesized via the polycondensation of resorcinol and formalin in alkaline medium in the presence of synthetic magnetite (10 wt %) with subsequent solidification at $210\text{ }^\circ\text{C}$. The coercive force of RFR-M at 300 K was 0.8 kA/m . The synthesis and characterization of the composite sorbent RFR-M are described in [23]. The 0.2–0.25 mm fraction of a bulk density of 0.59 g/cm^3 was used.

A model iron oxide labeled with ^{57}Co was synthesized as follows: 50 mL of 0.5 M FeSO_4 solution spiked with $^{57}\text{CoCl}_2$ was added to 100 mL of 0.5 M FeCl_3 solution, and then 3% ammonia hydroxide was added dropwise to reach pH 9. After stirring for 20 min, the colloidal solution was kept for 12 h, and then the precipitate was separated and washed with distilled water using a Buechner funnel. The precipitate was dried at $50\text{ }^\circ\text{C}$ until constant weight, crushed in a mortar, and sieved to obtain a 0.1–0.05 mm fraction. The activity of the sample was $42.7 \times 10^3\text{ Bq/g}$. Phases of magnetite (Fe_3O_4) and goethite ($\text{FeO}(\text{OH})$) were found in the iron oxide synthesized under the same conditions without a ^{57}Co tracer.

Porous hematite to be used as a catalyst for hydrothermal oxidation (HTO) was synthesized by the sol-gel method using siloxane-acrylate latex as a template. The synthesis was performed as follows: 40 mL of 0.5 M FeCl_3 solution was added to 200 mL of KE 13–36 emulsion with a latex content of 5%, and then 60 mL of 2 M NaOH solution was added dropwise until $\text{Fe}(\text{OH})_3$ formation. After 30 min of mixing followed by the precipitate sedimentation, $\text{Fe}(\text{OH})_3$ gel was separated using a “blue ribbon” filter paper, washed with distilled water, and dried at 90 °C; for 2 h until xerogel formation. The organic template was removed via xerogel annealing at 900 °C; for 1 h in an air atmosphere. The material obtained was crushed in a mortar, washed with distilled water to separate the fine fraction by decantation, and dried at 90 °C. The fraction of a size of 0.25–0.5 mm and a bulk density of 0.9 g/cm³ was used as an HTO catalyst.

2.2. SIER Decontamination Using Alkaline Deactivation Solution (DS)

2.2.1. SIER Decontamination Using Alkaline DS under Static Conditions

The decontamination of SIER with alkaline DS (2.25 mol/L NaNO_3 , 0.75 mol/L NaOH) under static conditions was performed in hermetically sealed 250 mL polypropylene vials as follows: 50 mL of the DS was added to 5 mL of SIER placed in vial no. 1; after mixing dispersion at 50 rpm for 20 h, the DS was removed with the pipette and transferred to vial no. 2, and then the activities of the SIER and DS were measured. In the next cycle, a fresh portion of the DS (50 mL) was added to SIER in vial no. 1. The full cycle of decontamination and activity measurements was repeated 5 times, and the total volume of DS used was 250 mL.

2.2.2. RFR-M-Assisted SIER Decontamination Using Alkaline DS under Static Conditions

The decontamination of SIER in the presence of RFR-M was performed in two cycles using 250 mL vials and an alkaline DS as described in Section 2.2.1. In the first cycle, 50 mL of the DS was added to four no. 1 vials containing 1, 2, 5, and 5 mL of SIER and 0.1, 0.1, 0.25, and 0.1 g of RFR-M, respectively. After shaking dispersions at 50 rpm for 20 h, RFR-M was localized in the bottom near the vial wall using a flat permanent magnet, and then pulp (the SIER and DS mixture) was accurately removed and transferred to no. 2 vials. Thereafter, DSs were removed from no. 2 vials with a pipette and transferred to no. 3 vials. After measuring activity in vials no. 1–3, DSs were returned to the no. 2 vials (with partially decontaminated SIER), and fresh portions of RFR-M of the same weight as in the first cycle were added. Mixing, separation, and activity measurements were performed as described for the first cycle.

2.2.3. SIER Decontamination Using Alkaline DS under Dynamic Conditions

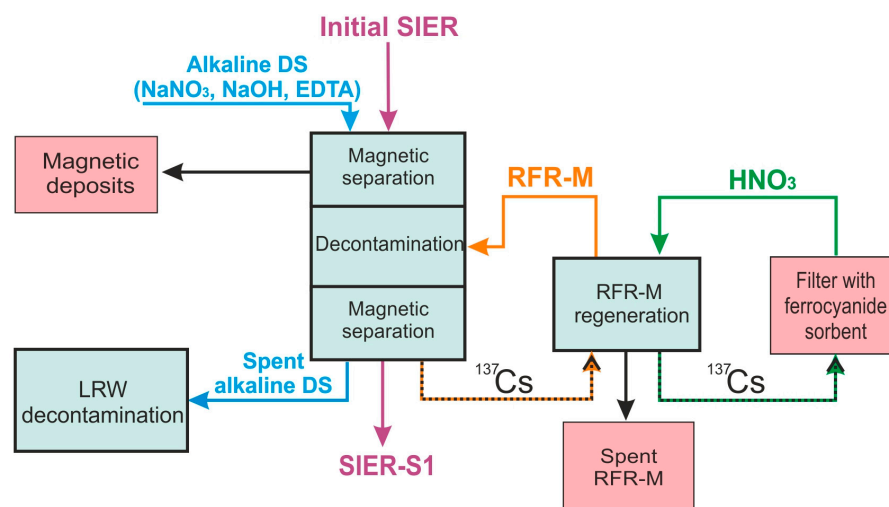
A total of 150 mL of a DS of the same composition as given in Section 2.2.1 was used for SIER decontamination under dynamic conditions as follows: 5 mL of SIER was placed in a sorption column with an inner diameter of 10 mm, then DS was fed at a flow rate of 1 mL/min, and eluate aliquots were taken every 25 mL for activity measurements.

2.3. SIER Decontamination Using Alkaline DS (Scheme 1)

2.3.1. RFR-Assisted SIER Decontamination

To separate the magnetic fraction, 100 mL of an alkaline DS (2.25 mol/L NaNO_3 , 0.75 mol/L NaOH, and 0.02 mol/L EDTA) was added to 10 mL of SIER in a polypropylene vial with a flat magnet mounted to the wall. After stirring the dispersion for 5 h, magnetic particles, SIER, and the DS were sequentially separated for activity measurement as described in Section 2.2.2. Then, the DS was returned to the vial with SIER, and three cycles of decontamination were performed in the presence of RFR-M as described in Section 2.2.2. Fresh portions (0.4 g) of RFR-M were used in the 1st and 2nd cycles. In the 3rd cycle, RFR-M, regenerated with nitric acid as described in Section 2.3.2 after the 1st cycle, was used. Thus, the final ratio (mL:mL:g) of SIER:DS:RFR-M after three cycles of decontamination was 10:100:0.8. After the 3rd cycle, the DS was separated and additionally decontaminated

using RFR-M collected in the 2nd cycle and regenerated with nitric acid. SIER was further decontaminated using an acidic DS as described in Section 2.4.



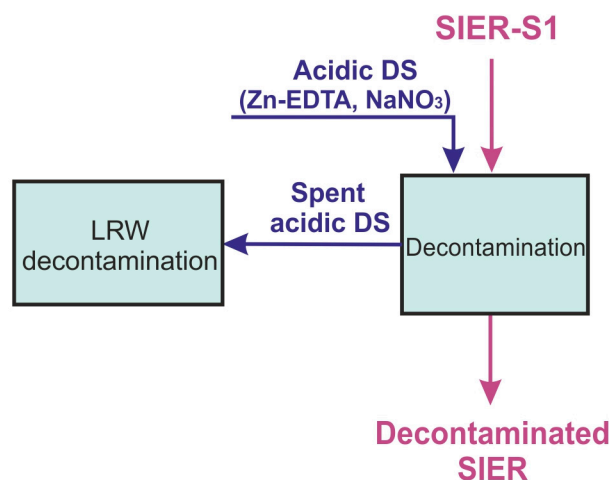
Scheme 1. RFR-assisted SIER decontamination using alkaline DS.

2.3.2. RFR-M Regeneration

The regeneration of RFR-M was performed under static conditions as follows: 5 mL of 0.5 M HNO_3 solution was added to 0.4 g of RFR-M and kept for 30 min under stirring. The procedure was repeated 4 times with fresh portions of the eluent. Nitric acid containing ^{137}Cs radionuclides was decontaminated in a column with an inner diameter of 6 mm filled with 1 mL of FNK-50 sorbent, and the flow rate was varied in the range of 3.5–13 bed volumes (BV/h) to optimize sorption conditions.

2.4. SIER Decontamination Using Acidic DS (Scheme 2)

A total of 25 mL of an acidic DS containing 0.05 mol/L ZnNO_3 , 0.05 mol/L $\text{Na}_2\text{H}_2\text{EDTA}$, and 2 mol/L NaNO_3 (pH 1.2) was added to 10 mL of SIER decontaminated as described in Section 2.3.1. After 20 min of contact under constant stirring, the DS was separated, and the activities of the SIER and DS were measured. Then, a fresh portion of the DS was added to a vial with SIER. Six cycles of decontamination were conducted with a total DS volume of 150 mL.



Scheme 2. SIER decontamination using acidic DS.

2.5. ^{57}Co Leaching from Model Iron Oxide Using Acidic DS

^{57}Co leaching from model iron oxide was investigated as follows: 0.05 g of iron oxide was brought in contact with 25 mL of solutions 0.05 M EDTA, 0.05 M Zn-EDTA, and 0.01 M Zn-EDTA under constant stirring. Zn-EDTA solutions were prepared by mixing $\text{Na}_2\text{H}_2\text{EDTA}$ and $\text{Zn}(\text{NO}_3)_2$ solutions at an equimolar ratio. In 5 days, the activities of the solution and iron oxide were measured after the phase separation by centrifugation.

2.6. Decontamination of Liquid Radioactive Wastes (LRWs) Generated during SIER Decontamination

LRWs generated after SIER decontamination, i.e., spent acidic DS (Scheme 2) or a mixture of spent alkaline DS (Scheme 1) and spent acidic DS (Scheme 2), were decontaminated from ^{60}Co radionuclides in a flow-type hydrothermal installation with a stainless steel reactor with an inner diameter of 8 mm (Figure 1). A total of 1 mL of the catalyst, obtained as described in Section 2.1.4, was placed in the maximal heat zone (the catalyst beads were fixed using the stainless cage with a rod thickness of 0.1 mm and mesh size of 0.05 mm). LRWs and an oxidizer (3% H_2O_2) were fed into the reactor separately using high-pressure Shimadzu LC-20AT chromatography pumps at flow rates of 0.25–0.75 mL/min and 0.25 mL/min, respectively. Hydrothermal oxidation was performed at a pressure of 10 MPa and a temperature of 190–240 °C; to determine the optimal temperature and flow rate. The outlet solution was collected, the γ -activity of 10 mL aliquots of inlet and outlet solutions were measured, and the values were recalculated taking into account dilution in the reactor.

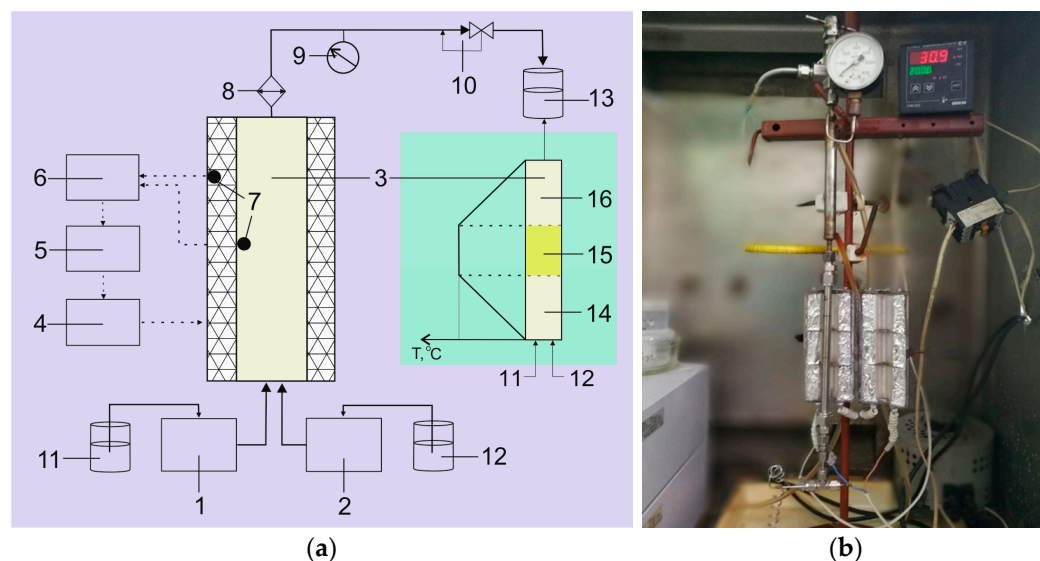


Figure 1. (a) Scheme of the laboratory installation for hydrothermal oxidation: 1 and 2—high-pressure pumps, 3—hydrothermal reactor, 4—single-phase power transformer, 5—automatic voltage regulator, 6—heat regulator, 7—thermocouples, 8—flow-type water cooler, 9—pressure gauge, 10—high-pressure relief valve, 11—vessel with contaminated solution, 12—vessel with hydrogen peroxide, and PV—receiver vessel. Insert: 14—heating zone, 15—zone of the catalyst location, and 16—cooling zone. (b) Photo of the laboratory installation for hydrothermal oxidation.

Then, LRW was decontaminated from ^{137}Cs radionuclides in a column with an inner diameter of 6 mm filled with 1 mL of Termoksid-35 sorbent at a flow rate of 15 BV/h.

2.7. Methods of Analysis

Radionuclide composition and specific γ -activities were determined using an AT 1315 Gamma–Beta spectrometer with a 63×63 mm NaI (Tl) detector (ATOMTEX, Minsk, Belarus) and multichannel gamma-spectrometer CANBERRA with a high-purity germanium semiconductor detector of the SEGe series and Genie-2000 software (Canberra Industries, Inc., Meriden, CT, USA).

Gamma (γ) spectra were recorded using an AT 1315 Gamma–Beta spectrometer with a 63×63 mm NaI (Tl) detector (ATOMTEX, Minsk, Belarus).

The specific activity of ^{57}Co (photopeak energy: 122 keV) leached from the model iron oxide was determined by the direct radiometric method using an RKG-AT1320 gamma-radiometer equipped with a NaI(Tl) detector measuring 63×63 mm (ATOMTEX, Minsk, Belarus).

Micrographs of the SIER surface were taken, and elemental analysis was performed using a Hitachi TM-3000 scanning electron microscope (Hitachi, Japan) with a Bruker energy dispersive X-ray spectrometer detector (Bruker Nano GmbH, Germany).

The elemental composition of deposits was determined by energy-dispersive X-ray fluorescence spectroscopy using a Shimadzu EDX-800-HS spectrometer equipped with an X-ray tube with Rh-anode.

X-ray diffraction spectra were recorded using a D8 Advance diffractometer (Bruker, Germany).

UV-vis spectra were recorded using a Shimadzu 1650PC scanning UV-vis spectrophotometer (Shimadzu, Japan).

3. Results and Discussion

3.1. SIER Characterization

An SEM investigation has revealed an inorganic nature of the fine fraction, which was mechanically separated from SIER beads or deposited at the beads' surface (Figure 2). Due to the inhomogeneity of inorganic particle distribution, the specific activity of different SIER samples varied, but the average specific activity was about 3×10^4 Bq/g, with the main contributions from ^{137}Cs -137 (3×10^4 Bq/g), ^{60}Co (3×10^3 Bq/g), and ^{94}Nb (7×10^2 Bq/g) radionuclides.

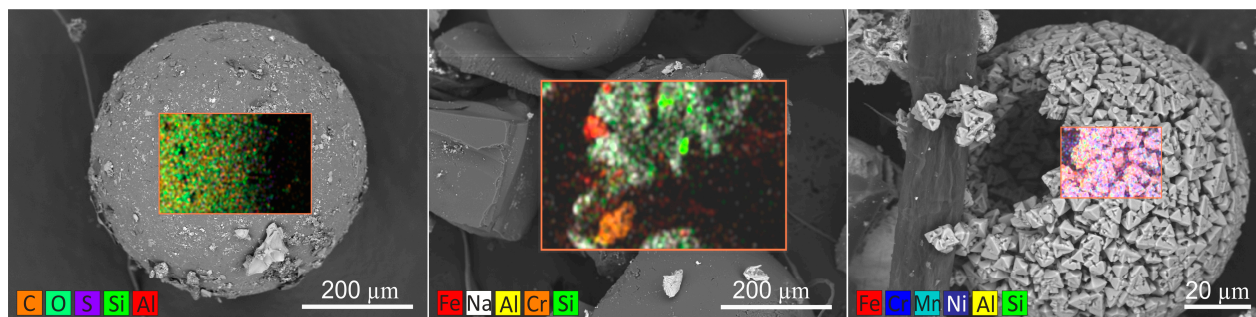


Figure 2. SEM images and elemental mapping of SIER beads and particles of inorganic deposits.

To investigate the nature of the inorganic deposits, the magnetic fraction was separated from a dry SIER sample using a flat magnet and analyzed by X-ray fluorescence spectroscopy: the following elemental composition was found (%): Fe—76, Si—10, Al—3.8, S—2.1, Zr—2.1, Na—1.8, K—0.96, Cr—0.82, Cu—0.81, Ca—0.48, Mn—0.26, Ni—0.25, Ti—0.17, Zn—0.07, Nb—0.03, and Sr—0.02. These data suggest that SIER was contaminated with silicate and corrosive deposits (crud from the active zone) as well as fragments of fuel element claddings (Zr and Nb). The specific activity of deposits was ^{137}Cs — 27.5×10^3 Bq/g, ^{60}Co — 64.3×10^3 Bq/g, and ^{94}Nb — 5×10^3 Bq/g, which indicates the relatively homogeneous distribution of ^{137}Cs activity between organic and inorganic phases, while ^{60}Co and ^{94}Nb radionuclides were concentrated in the deposits. Thus, efficient mechanical separation or solubilization of the deposits from the SIER matrix is required to reach high decontamination factors and lower the class of waste.

3.2. RFR-Assisted SIER Decontamination from ^{137}Cs Radionuclides Using Alkaline Solutions

We have previously shown that alkaline NaNO_3 deactivation solutions (DSs) were efficient to release cesium radionuclides from silicate deposits in low-level-activity SIER samples [23,24]. Here, the feasibility and efficiency of this strategy for the decontamination of intermediate-level-activity SIER from an NPP storage tank were evaluated. Preliminary

experiments (Table 1) have shown that washing SIER with an alkaline DS provides an efficiency of ^{137}Cs removal of up to 96.3%.

Table 1. Efficiency (%) of ^{137}Cs removal from SIER with dependence on decontamination method and DS: SIER ratio (mL:mL). DS composition—2.25 mol/L NaNO_3 and 0.75 mol/L NaOH .

Decontamination Method *	DS:SIER Ratio				
	10	20	30	40	50
Static conditions (2.2.1)	61	75	80	82	82
Dynamic conditions (2.2.3)	89	95.5	96.3	-	-
Static conditions + 0.5 g RFR-M (2.2.2)	99.8	-	-	-	-

* Corresponding section of the experimental part with detailed description of the decontamination method is given in parentheses.

The addition of sorbents selective to cesium ions to the alkaline DS at this stage is beneficial to shift the equilibrium of cesium distribution between SIER and the deactivation solution, i.e., to prevent readsorption of the released cesium ions on SIER, which increases the decontamination factor [23]. Since the application of highly selective ferrocyanide-based sorbents is limited by their low chemical stability at $\text{pH} > 12$ [25], resorcinol-formaldehyde resins (RFRs) with high chemical stability [26] and high selectivity to cesium ions [27] in highly mineralized alkaline media can serve as an alternative. Indeed, in the presence of RFR, which concentrates ^{137}Cs radionuclides released from SIER, the efficiency of ^{137}Cs removal increased up to 99.8% at a significantly lower volume of the alkaline DS (Table 1).

To solve the problem of SIER and RFR separation, magnetite-containing composite resin (RFR-M) was synthesized and used. Since the idea of RFR-assisted SIER decontamination is based on the shift of the cesium distribution equilibrium, the efficiency of ^{137}Cs transfer from SIER to RFR-M will be determined by the competition of different processes characterized by different distribution coefficients (K_d), i.e., $K_{d(\text{silicate}/\text{DS})}$, $K_{d(\text{SIER}/\text{DS})}$, and $K_{d(\text{RFR-M}/\text{DS})}$, and, thus, by the SIER:DS:RFR-M ratio [23]. The effect of the selected SIER:DS:RFR-M ratios on the residual activity of ^{137}Cs in SIER has shown (Table 2) that an increase in RFR-M:DS and RFR-M:SIER ratios facilitates ^{137}Cs transfer from SIER to RFR-M. A significant reduction in the ^{137}Cs residual activity was attained already after the first cycle of SIER washing with an alkaline DS, and this result was improved in the 2nd cycle with a maximal efficiency of cesium removal of up to 99.96%.

Table 2. Residual ^{137}Cs activity (%) on SIER after RFR-M-assisted decontamination at different SIER:DS:RFR-M (mL:mL:g) ratios (see Section 2.2.2 for details).

SIER:DS:RFR-M *	1:50:0.2	2:50:0.2	5:50:0.5	5:50:0.2
1st cycle	0.4	0.98	1.2	3.9
2nd cycle	0.04	0.08	0.2	1.2

* Total weight of RFR-M after two cycles of decontamination in alkaline DS.

To minimize the volume of the secondary wastes, RFR-M can be regenerated with acidic solutions and reused. It was earlier shown that selective sorption characteristics of RFR toward ^{137}Cs radionuclide in highly mineralized alkaline solutions insignificantly decreased in several sorption/regeneration cycles [23,28,29].

The general scheme used in the feasibility study of intermediate-level-activity SIER decontamination from ^{137}Cs radionuclides is shown below (Scheme 1). Although a significant part of SIER magnetic deposits containing ^{60}Co and ^{94}Nb can be virtually removed at the stage of SIER/RFR-M magnetic separation, it is not recommended, since the accumulation in RFR-M of insoluble in HNO_3 impurities can negatively affect the RFR-M performance in consecutive sorption/regeneration cycles. Thus, we suggest performing magnetic separation of the deposits after the swelling of SIER in an alkaline DS but before RFR-M addition.

Scheme 1 was applied for the decontamination of the SIER sample (volume of 10 mL, weight of 8.7 g, and specific activities: ^{137}Cs 2.7×10^4 Bq/g, ^{60}Co 3.1×10^3 Bq/g, and ^{94}Nb 7.6×10^2 Bq/g), and the γ -spectrum shown in Figure 3 (spectrum 1). Decontamination was performed as follows: 100 mL of an alkaline DS (DS:SIER ratio 10) of the above mentioned composition with the addition of 0.02 mol/L EDTA (EDTA was added to eliminate hydroxide precipitation) was prepared, and then magnetic particles were separated with a flat magnet. In this case, aside from the dissolution of silicate deposits, SIER swelling in alkaline medium facilitates the mechanical detachment of magnetic particles attached to the beads' surface, which, in comparison with "dry" magnetic separation, decreases the probability of capturing SIER beads with the shell of magnetic deposits. At the stage of "wet" separation, 30% of ^{60}Co , 76% of ^{94}Nb , and about 1% of ^{137}Cs were removed with magnetic particles (Figure 3, spectrum 2). About 20% of ^{137}Cs , 15% of ^{60}Co , and 2% ^{94}Nb relative to the initial activity were transferred from SIER to the alkaline DS. Separated magnetic particles varied in morphology and composition (Figure 4).

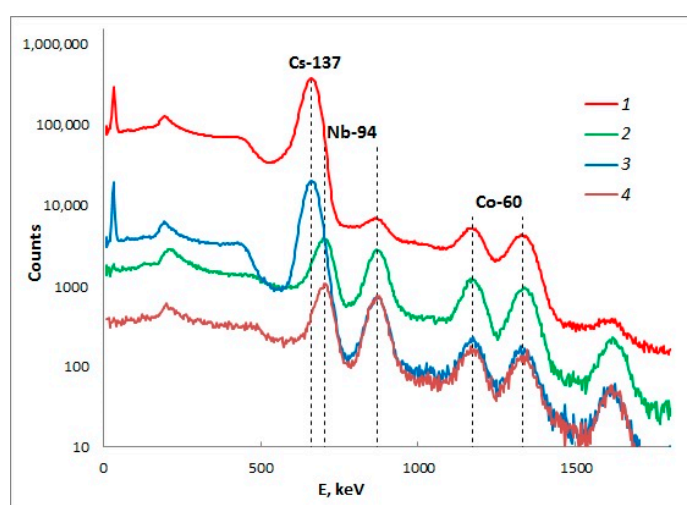


Figure 3. γ -spectra of initial SIER sample (1), magnetically separated deposits (2), and RFR-M after the 1st cycle of SIER decontamination before (3) and after (4) regeneration with 0.5 M HNO_3 .

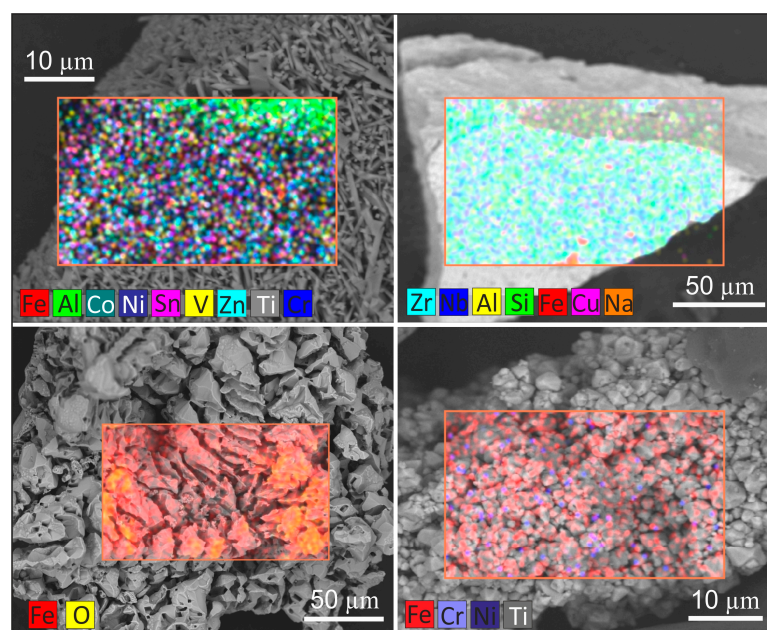


Figure 4. SEM images and elemental mapping of magnetic deposits on SIER.

After magnetic separation, RFR-M was added, and three cycles of RFR-M-assisted SIER decontamination using an alkaline DS were performed. The residual activity of the SIER was ^{137}Cs —127 Bq/g, ^{60}Co —1520 Bq/g, and ^{94}Nb —95 Bq/g, which corresponds to 0.46, 49, and 12.5% relative to the initial activity of SIER, respectively. The efficiency of cesium radionuclides elution from RFR-M with 0.5 M nitric acid was very high, whereas contamination with corrosion radionuclides was insignificant due to the preliminary magnetic separation of magnetic deposits (Figure 3, spectra 3 and 4). Nitric acid with a specific ^{137}Cs activity of 3.8×10^6 Bq/L was decontaminated using selective sorption on a ferrocyanide sorbent, FNK-50, under dynamic conditions at a flow rate of 3.5 BV/h. The activity of the decontaminated HNO_3 solution was 860 Bq/L, which corresponds to a decontamination factor of 4.4×10^3 . This confirmed the possibility of cyclic HNO_3 usage in Scheme 1; however, periodical adjustment of its concentration may be required due to the H^+ consumption for RFR-M regeneration.

3.3. SIER Decontamination from Radionuclides Entrapped in Metal Oxide Deposits

Despite the high efficiency of Scheme 1 for cesium removal from SIER, ~49% of ^{60}Co activity remained in the resin. ^{60}Co removal was achieved mostly via the preliminary magnetic separation stage and the cocapture of ^{60}Co -containing crud during SIER/RFR-M separation (Figure 3, spectra 2 and 4). The remaining ^{60}Co activity in SIER was probably located in deposits, which cannot be separated magnetically. For instance, iron-containing particles were still found in SIER after decontamination with the alkaline DS (Figure 5). Thus, modification of Scheme 1 was required to increase the efficiency of intermediate-level-activity SIER decontamination.

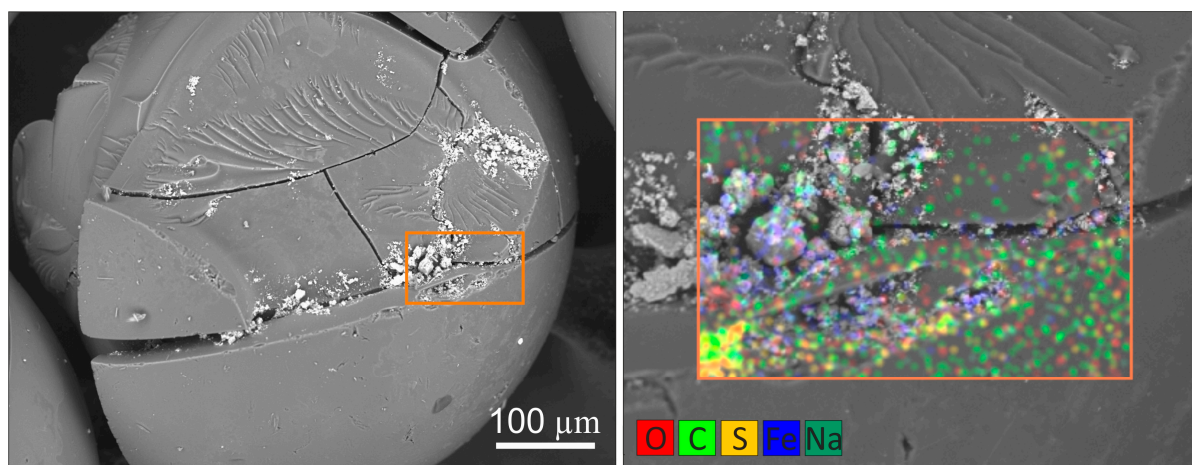


Figure 5. SEM images and elemental mapping of deposits on SIER after decontamination with alkaline DS.

To release ^{60}Co from SIER, organic acids with good chelating properties, such as oxalic, citric, and ascorbic acids as well as aminopolycarboxylic acids, are more appropriate alternatives to mineral acids, which are characterized by higher corrosion activity and lower potential to leach cobalt radionuclides from the iron oxide phase [13,30]. Among organic acids, EDTA is the best choice to meet the criteria of stability in nitrate solutions (nitrates are added to deactivation solutions to prevent readsorption of the anionic complexes on anion-exchangers during the decontamination of SIERs from mixed-bed filters [31]) and the ability to chelate transition metal ions, including corrosion radionuclides. Logarithms of stability constants of EDTA complexes are 16.4 and 41.4 with Co(II) and Co(III) ions, respectively, and 14.3 and 25 with Fe(II) and Fe(III) ions, respectively [32]. EDTA and its salt solutions, mostly Na_2EDTA , are used in nuclear power facilities to remove corrosion products from construction materials and cation-exchangers.

The dissolution of iron (oxy)hydroxide is known to be promoted at lower pH. However, the addition of inorganic acids to EDTA salt solutions results in the precipitation of poorly soluble EDTA on the SIER surface (the minimum of EDTA solubility falls into a pH range of 1.6–2) [33,34]. Avoiding EDTA precipitation at low pH is possible when deactivation solutions contain EDTA complexes with metal ions. In this case, upon complex formation, the pH decreases as a result of H^+ release from EDTA. For instance, the usage of Zn-EDTA solution enhances the release of cobalt radionuclide from synthetic iron oxide labeled with ^{57}Co (Table 3). One can see that the dissolution process is accompanied by the consumption of H^+ and proceeds more efficiently in Zn-EDTA than in Na_2EDTA solution.

Table 3. Leaching ^{57}Co from the model iron oxide (see Section 2.1.4 for the synthesis) at solid:liquid ratio of 1:500.

Solution	pH ₀	^{57}Co in Solution, %	pH _{eqv}
Na_2EDTA 0.05 M	4.4	19.7	5.9
Zn-EDTA 0.05 M	1.8	80.2	2.4
Zn-EDTA 0.01 M	2.2	20.8	3.9

Thus, the SIER sample decontaminated using Scheme 1 (labeled SIER-S1) can be further treated with an acidic solution containing the complex of Zn(II) with EDTA (Scheme 2). The advantage of this complex is determined by the amphoteric nature of Zn^{2+} ions, which prevents the formation of insoluble hydroxides at a high pH.

The decontamination of the SIER-S1 sample with an acidic DS, containing 0.05 mol/L Zn-EDTA and 2 mol/L $NaNO_3$, was performed in six steps, using, in each step, a fresh DS aliquot at a DS:SIER ratio of 2.5:1 (v/v) to elucidate decontamination kinetics in acidic medium. The release of radionuclides to the DS occurred stepwise (Table 4): ^{137}Cs radionuclides were mainly detected in the first aliquot (pH was 8.9 as a result of the neutralization of the acidic DS with the alkaline DS from the swollen SIER), and a further decrease in pH resulted in the release of ^{60}Co ; moreover, an intensive blue color of the second aliquot typical for Cu(II) complexes indicated possible desorption of Cu(II) ions from SIER-S1 (Figure 6, Table 4). The γ -spectrum of the solution obtained by mixing aliquots 1–6 is shown in Figure 7, spectrum 1. Subsequent treatment with 2.25 M $NaNO_3$ solution or an aliquot of a fresh alkaline DS followed by an aliquot of the acidic DS had no effect on the SIER residual activity. The specific residual activity of decontaminated SIER was 16.9 Bq/g, with a 6.9 Bq/g of ^{137}Cs , 4.1 Bq/g of ^{60}Co , and 5.9 Bq/g of ^{94}Nb , and its γ -spectrum is shown in Figure 7, spectrum 2. Thus, SIER decontamination factors after treatment using Schemes 1 and 2 were $>10^3$ for ^{137}Cs and $>10^2$ for ^{60}Co and ^{94}Nb .

Table 4. Radionuclide distribution in acidic DS aliquots with DS:SIER-S1 ratio of 2.5:1 (mL/mL).

Aliquot No.	Radionuclide Content, %		pH
	^{137}Cs	^{60}Co	
1	41.9	2.1	8.9
2	18.7	40.5	2.76
3	17.3	31.7	1.87
4	13	12.4	1.38
5	6.1	10.3	1.36
6	3.0	3.0	1.34

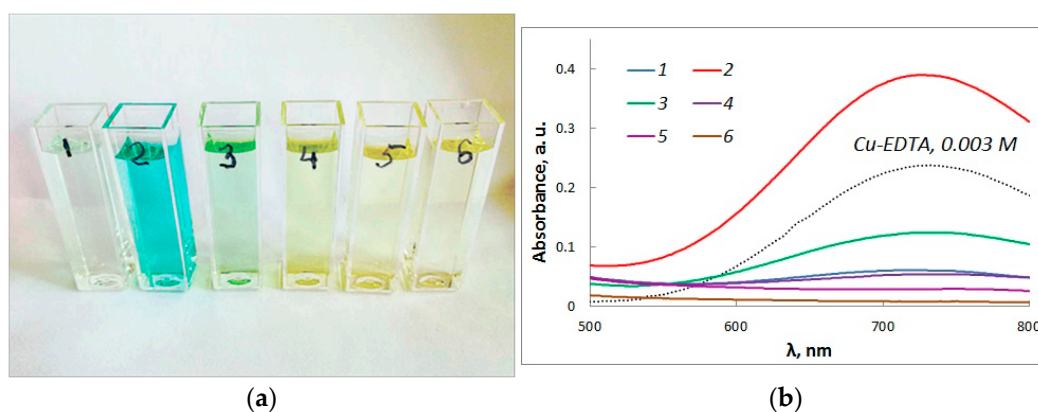


Figure 6. Photo (a) and UV-vis spectra (b) of acidic DS after stepwise SIER-S1 decontamination.

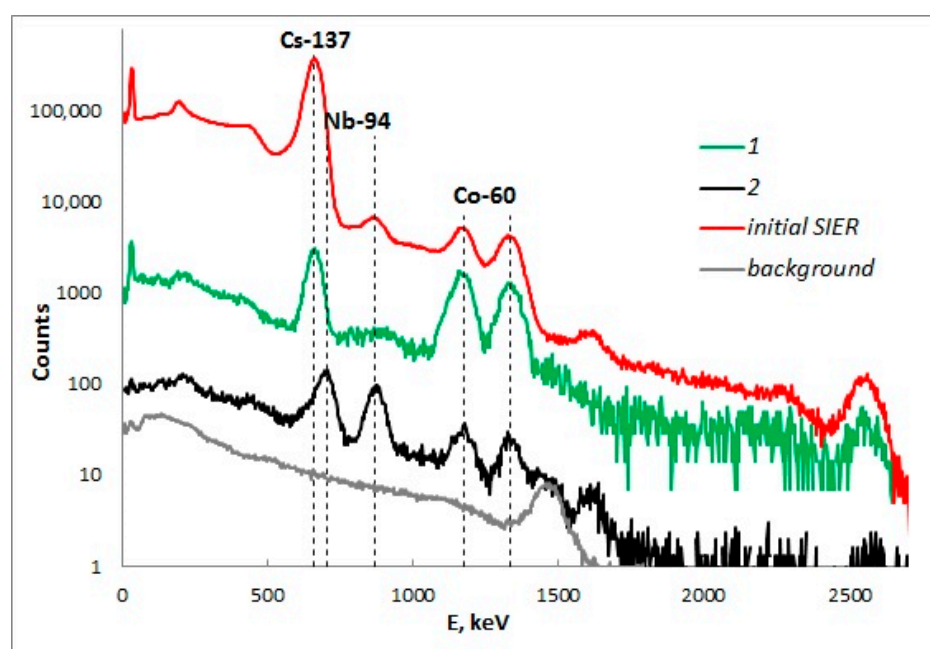


Figure 7. γ -spectra of acidic DS after SIER-S1 decontamination (1) and of decontaminated SIER (2). Spectra of initial SIER sample and background are given for comparison.

3.4. Decontamination of Liquid Radioactive Wastes (LRWs) Generated during SIER Decontamination

LRW generated in the process of SIER decontamination, including spent alkaline DS (Scheme 1) and spent acidic DS (Scheme 2), must be processed to safely immobilize radionuclides in solid matrices.

Spent acidic DS was contaminated with ^{60}Co -EDTA complexes, which are very stable under normal conditions. Since the removal of radionuclides from this type of LRW is complicated, usually, methods known as advanced oxidation and targeted to the destruction of the organic part of the complex are used in combination with subsequent ^{60}Co sorption or precipitation [35–37]. A promising method of such wastes processing consists of hydrothermal oxidation (HTO) using hydrogen peroxide as an oxidizer in the flow-type installation. After the destruction of the complexes, cobalt radionuclides remained in the reactor of HTO installation in the form of oxide Co_3O_4 . The mechanism of Co-EDTA destruction under hydrothermal conditions was discussed earlier [38]: the chelate structure degrades as a result of the electron transfer from the ligand to Co(III), while the hydrogen peroxide is responsible for the generation of Co(III) from Co(II) and oxidation of organics not bound to complexes. The application of transition metal (iron, manganese, and nickel) oxides as catalysts increases the Co-EDTA decomposition rate and decreases the temperature of

the HTO process [39]: ^{60}Co radionuclides in this case are immobilized in a newly formed oxide phase of the catalyst. Thanks to the very low cobalt leaching rate from the formed oxides ($<10^{-6} \text{ g/cm}^2 \cdot \text{day}$), the HTO reactor with a spent catalyst can be considered a solid radioactive waste (SRW) ready for disposal [40–42].

Hydrothermal oxidation of spent acidic DS was performed with 1 M H_2O_2 solution. Figure 8 shows the γ -spectra of the initial solution (spectrum 1) and the solution after HTO at 220 °C; at a volumetric ratio of LRW: H_2O_2 flow rates of 0.5:0.25 (spectrum 2). Further decontamination of the outlet solution using the ferrocyanide sorbent Termoksid-35 provides efficient removal of ^{137}Cs radionuclides (Figure 8, spectrum 3).

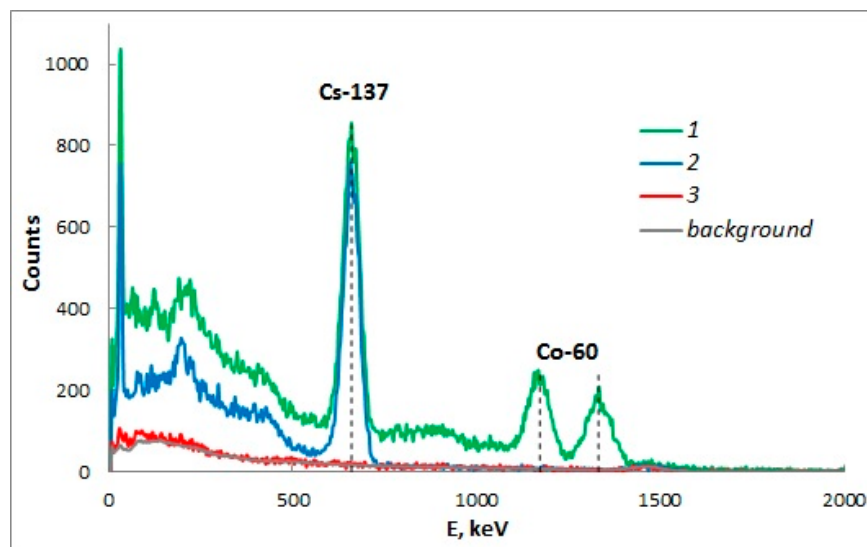


Figure 8. γ -spectra of spent acidic DS (pH 2.12) before purification (1), after HTO at 220 °C; at volumetric flow rates of 1 M H_2O_2 and LRW of 0.25 mL/min and 0.5 mL/min, respectively (2), and after post-treatment using Termoksid-35 sorbent (3).

Spent alkaline DS was contaminated with ^{137}Cs radionuclides, since RFR-M did not provide complete removal of ^{137}Cs under static sorption conditions. Since EDTA was added to the solution to prevent hydroxide precipitation in Scheme 1, spent alkaline DS also contained ^{60}Co -EDTA complexes. Moreover, alkaline solutions after long-term contact with RFR contain products of RFR oxidative destruction, which is enhanced from one application cycle to another [43]. Therefore, an appropriate purification scheme for such solutions is the same as for the spent acidic DS, i.e., HTO and post-treatment with ferrocyanide sorbent. This approach can be applied to spent alkaline DS and their mixtures with spent acidic DS.

Figure 9 shows the γ -spectrum of an aliquot of the LWR obtained by mixing spent alkaline and acidic DSs with a final pH 9.5 (spectrum 1) and the result of its decontamination by HTO at 220 °C; at a volumetric ratio of LRW: H_2O_2 flow rates of 0.5:0.25 (spectrum 2). When the volumetric ratio was increased to 0.75:0.25, complete removal of ^{60}Co was not attained (spectrum 3). The decrease in the decontamination efficiency is related to both the decrease in the oxidizer concentration and the increase in the cumulative flow rate of the mixture in the reactor. The advantage of the flow-type HTO installation consists of the possibility to tune the flow rates of LRW and the oxidizer, as well as the temperature, to attain the required decontamination factor. Post-treatment of the solution decontaminated by HTO using a column with Termoksid-35 sorbent provided activity reduction down to the background level (Figure 9, spectrum 4).

As was shown above, both types of LRW contained complexes of EDTA and cesium radionuclides. It is worth mentioning that the decontamination of such LRW from ^{137}Cs on selective inorganic sorbents should be performed after HTO, since the presence of EDTA in solutions can lead to the decomposition of ferrocyanides due to the binding of metal

ions from the sorbent phase by EDTA with the formation of stable complexes. This is evident from the emergence of absorption bands typical for a Ni-EDTA complex in the electronic spectra of LRW passed through Termoksid-35 (Ni-K ferrocyanide) without HTO pretreatment (Figure 10).

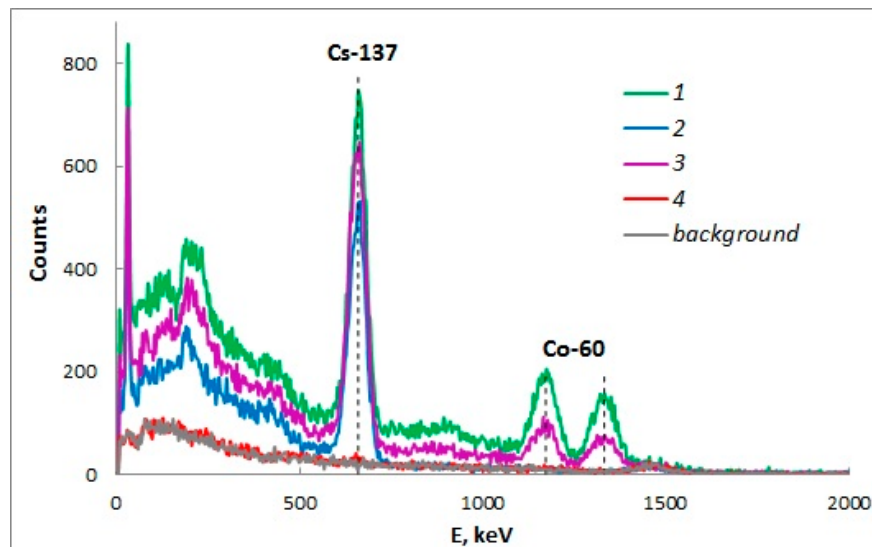


Figure 9. γ -spectra of LRW with pH 9.5 before purification (1), after HTO at 220 °C; at volumetric flow rates of 1 M H_2O_2 of 0.25 mL/min and of LRW of 0.5 (2) and 0.75 (3) mL/min, and after post-treatment using Termoksid-35 sorbent (4).

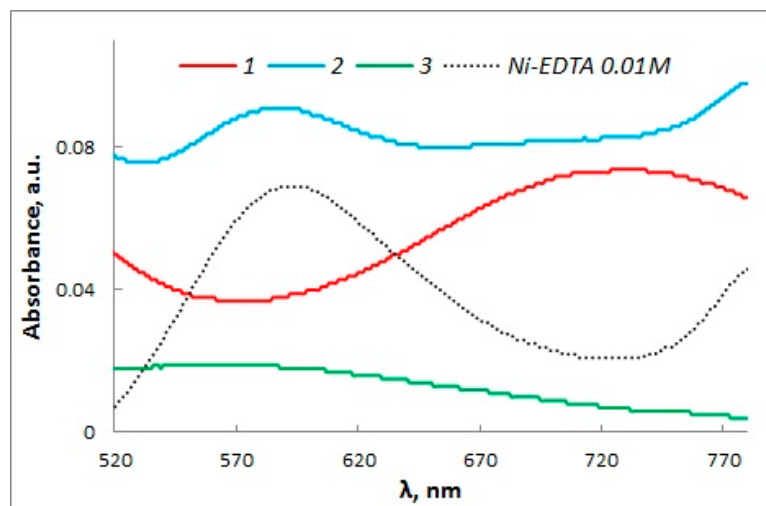


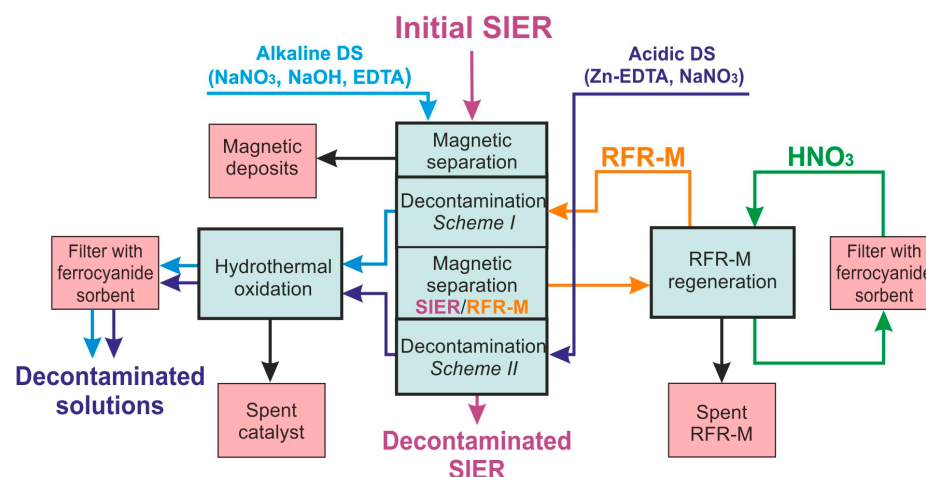
Figure 10. Electronic spectra of LRW obtained by mixing spent alkaline and acidic DSs before (1) and after filtration through Termoksid-35 without (2) and with (3) HTO pretreatment. Electronic spectra of 0.01 M Ni-EDTA solution is given for comparison.

To sum up, it can be concluded that LRW formed in the SIER decontamination process can be decontaminated by a combination of HTO and selective sorption to the level at which we can consider them nonradioactive wastes.

3.5. The Optimized Scheme of SIER Decontamination

Based on the results obtained, an optimized SIER decontamination scheme was suggested (Scheme 3). This scheme was obtained by the supplementation of Scheme 1 (RFR-assisted alkaline decontamination) with acidic decontamination (Scheme 2) and with an LRW treatment unit combining HTO and selective sorption in a column with a ferrocyanide

sorbent. The contributions of each stage to the overall SIER decontamination efficiency are summarized in Table 5. The decontamination factors for ^{137}Cs , ^{60}Co , and ^{94}Nb radionuclides were 3.9×10^3 , 7.6×10^2 , and 1.3×10^2 , respectively, and the activity of the decontaminated SIER was 17 Bq/g. According to the Classification of Radioactive Wastes, this residual activity is higher than that of exempt waste (EW), which is a few Bq/g, but meets criteria of very low-level waste (VLLW) [44], which do not need a high level of containment and isolation and, therefore, are suitable for disposal in near-surface landfill-type facilities with limited regulatory control [45].



Scheme 3. The optimized scheme of SIER decontamination.

Table 5. Specific activities (Bq/g) of the air-dry SIER decontaminated using Scheme 3.

	^{137}Cs	^{60}Co	^{94}Nb	Σ
Initial SIER	2.7×10^4	3.1×10^3	7.6×10^2	3.1×10^4
SIER after wet magnetic separation	2.1×10^4	1.7×10^3	1.7×10^2	2.3×10^4
SIER after RFR-assisted decontamination using alkaline DS	127	1.5×10^3	95	1.7×10^3
SIER after decontamination using alkaline and acidic DS	6.9	4.1	5.9	1.7×10^1

3.6. Solid Radioactive Wastes Generated after SIER Decontamination

Solid radioactive wastes (SRWs) formed as a result of SIER decontamination using Scheme 3 include filters with ferrocyanide sorbents, a spent HTO catalyst, and powdered deposits magnetically separated from SIER. Spent RFR-M after cesium elution can be dissolved, and the solution formed can be further processed using HTO and selective sorption [43]; the insoluble inorganic fraction from RFR-M (synthetic magnetite and magnetic deposits) can be disposed of as SWR. As the volume of the decontaminated solutions significantly exceeds the volume of the sorbents and the catalyst used in this process, the reduction in the radioactive waste amount to be sent for the final disposal will be determined by the volumetric LRW/SRW ratio.

The radionuclide distribution between SRW types generated from the application of Scheme 3 to the decontamination of 10 mL of SIER is shown in Figure 11: ^{137}Cs is immobilized in ferrocyanide sorbents, ^{60}Co is immobilized in an HTO catalyst, and magnetic deposits contain ^{60}Co and ^{94}Nb .

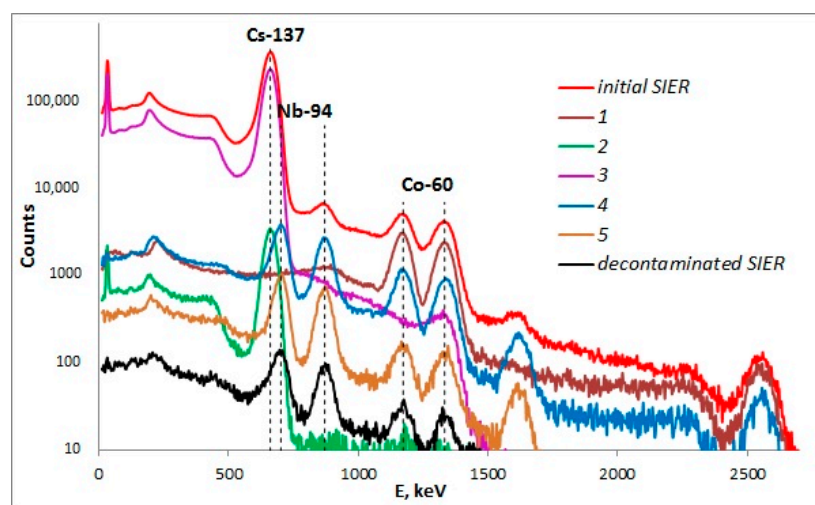


Figure 11. γ -spectra of solid wastes generated after decontamination of 10 mL of SIER: 1 mL of HTO catalyst (1), 1 mL of Termoksid-35 (2), 1 mL of FNK-50 sorbent (3), 0.1 g of magnetic deposits (4), and 0.8 g of spent RFR-M after regeneration with nitric acid (5). Spectra of initial and decontaminated SIER samples are given for comparison.

4. Conclusions

A feasibility study of decontamination of intermediate-level-activity spent ion-exchange resins (SIERs) from the Kursk NPP has been conducted with the primary objective to transfer SIER to the category of exempt waste (EW) or very low-level waste (VLLW) to reduce disposal costs. It has been shown that nonexchangeable radionuclides, which cannot be removed during resin regeneration, are concentrated in poorly soluble inorganic deposits represented by aluminosilicates, activated corrosion products, and fragments of the fuel element cladding. The suggested conceptual scheme of SIER decontamination included “wet” magnetic separation and sequential washing with alkaline and acidic deactivation solutions containing EDTA. Magnetic separation provided an efficiency of ^{94}Nb and ^{60}Co radionuclide removal of $\sim 77\%$ and $\sim 45\%$, respectively. The decontamination of SIER using an alkaline deactivation solution (2.25 mol/L NaNO_3 , 0.75 mol/L NaOH , and 0.02 mol/L EDTA) in the presence of magnetic resorcinol-formaldehyde resin (RFR-M) allowed the removal of $>99\%$ of ^{137}Cs radionuclides and a significant reduction in ^{94}Nb activity. ^{137}Cs radionuclides concentrated in RFR-M could be further eluted with nitric acid and immobilized in a ferrocyanide sorbent for disposal. SIER decontamination from ^{60}Co radionuclides, which are both ion-exchangeable and captured in poorly soluble deposits and were not separated magnetically, was conducted using acidic solutions containing Zn(II) -EDTA complexes, and the efficiency exceeded 99%. The activity removed from SIER was transferred to the inorganic solid matrices using selective sorption and hydrothermal oxidation (HTO), which provided an efficient reduction in the solid waste volume, virtually avoiding the generation of additional liquid radioactive wastes.

To sum up, the application of the suggested strategy allowed a decrease in the specific activity of the SIER sample from 3.1×10^4 (2.7×10^4 Bq/g of ^{137}Cs , 3.1×10^3 Bq/g of ^{60}Co , and 7.6×10^2 Bq/g of ^{94}Nb) to 16.9 Bq/g (6.9 Bq/g of ^{137}Cs , 4.1 Bq/g of ^{60}Co , and 5.9 Bq/g of ^{94}Nb), with the final decontamination factors above 10^3 and 10^2 for ^{137}Cs and ^{60}Co and ^{94}Nb , respectively. Although the decontaminated SIER did not meet criteria for EW (a few Bq/g), it can be considered VLLW (tens of Bq/g) [44] and, according to IAEA recommendations [45], is suitable for disposal in near-surface landfill-type facilities with limited regulatory control.

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