DEVELOPMENT OF A TECHNOLOGY FOR WWER-1200 STILL EVAPORATE CONCENTRATE FROM RADIONUCLIDES

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The paper presents a method developed to treat evaporate concentrates from WWER-1200 reactor units of the Novovoronezh NPP-2 and Leningrad NPP-2 providing the removal of the main dose-contributing radionuclides (^{7}Be, ^{59,63}Ni, ^{124,125}Sb, ^{137,134}Cs, ^{60}Co, ^{54}Mn, ^{110m}Ag) via sorption, precipitation, destructive and membrane treatment. The paper proposes a treatment flowchart involving ozonation, filtration, pH adjustment and treatment with the Termoksid-35 sorbent. The study indicates that the specific α- and β-activity of the resulting filtrate after its evaporation to dry salts accounted for <110 and 1000–3000 Bq/kg respectively, with the latter one explained by the presence of the natural ^{40}K isotope. Material balance assessment of this method showed that the volume reduction factors for the treated RW from Novovoronezh NPP-2 and Leningrad NPP-2 accounted for 132.6 and 36.4, respectively. When these two indicators were recalculated to the LRW volume with an average salt content of ~4 g/L, the calculated RW volume reduction factors amounted to ~3,900 and ~3,270, respectively.

Keywords: *liquid radioactive waste, NPP evaporate concentrates, ozonation, filtration, pH adjustment, sorption, Termoksid-35, radioactive waste.*

Introduction

Development of low-waste processing methods for liquid radioactive waste (LRW) from nuclear power plants (NPP) is highly relevant due to the large inventory of accumulated and newly generated waste of this type. During NPP operation, the main LRW stream accounts for evaporate concentrates (EC) resulting from the evaporation of various radioactive media (floor drains, regeneration and decontamination solutions, laundry water). Until recently, cementation, bituminization and deep evaporation methods were implemented to process EC at Russian NPPs. These methods convert the waste into an environmentally safe form but do not provide somewhat considerable reduction in terms of RW volumes requiring disposal.

In 2007, an ion-selective treatment unit (ISTU) providing LRW processing was commissioned at Kola NPP with similar units that have been operating at Smolensk NPP and Kursk NPP since 2017 and 2024 respectively. This unit provides ozonation, filtration to separate the resulting precipitate and sorption on ferrocyanide sorbent Termoksid-35 (T-35). Ozone destroys complexes and converts cobalt and manganese radionuclides into metal hydroxide precipitates, which are than separated by filtration. To recover cesium radionuclides, the

resulting filtrate is fed through the T-35 sorbent. After its subsequent deep evaporation, upon cooling, a solid salt residue (salt melt), which is not referred to the radioactive waste (RW) category, is formed. This process reduces the volume of the residue relative to the original EC by a factor of 80—100.

However, practice showed the ineffectiveness of this method in treating newly generated drain waters from new-generation NPPs such as the Novovoronezh NPP-2 (NVNPP-2) with a WWER-1200 reactor unit and the key radionuclides accounting for ^{7}Be, ^{124,125}Sb, ^{137,134}Cs, ^{60}Co and ^{54}Mn [1]. The problem of antimony isotope removal is associated with their presence in the EC both in soluble ionic forms and in the form of colloids and pseudocolloids, various complexes depending on the pH and chemical composition of the EC.

This study mainly explores the feasibility and conditions for the extraction of the main radionuclides contained in the EC from the Novovoronezh NPP-2 and Leningrad NPP-2 (LNPP-2) via sorption, precipitation, destructive and membrane methods.

Thus, the following activities were performed:

- Radionuclide distribution Kd and radionuclide treatment Ktr coefficients for the initial and oxidized EC were determined under static conditions in alkaline and acidic environments using promising selective sorbents;
- The EC was treated under dynamic conditions in alkaline and acidic environments using certain selected selective ion-exchange materials;
- the sorbent life was calculated;
- the treatment coefficients for the precipitation (coprecipitation) of radionuclides in EC were determined based on various collectors in alkaline and acidic environments;
- the required membrane rating enabling key radionuclide removal from the EC by microfiltration and ultrafiltration after oxidation was established;
- the effect produced by oxidation (complex destruction) and subsequent introduction of collectors on radionuclide sorption in EC under acidic alkaline environments was studied;
- a process flow chart providing radionuclide removal from EC was developed;
- the material balance for the WWER-1200 EC treatment method was assessed.

Peroxide oxidation and ozonation have been identified as most preferred destructive methods [2]—[4]: they do not generate additional secondary waste with the exception of sediments due to some macro-quantities (tens of mg/dm^3) of corrosion products found in the original EC.

Among the precipitation methods, coprecipitation on iron hydroxide acting as a collector for a large number of radionuclides, including ^{7}Be, ^{124}Sb, ^{125}Sb [7] appears a preferable option.

Among the sorption methods, the most optimal option accounts for the use of inorganic sorbents: relevant EC treatment experience has been accumulated with regard to such radionuclides as ^{134}Cs, ^{137}Cs, ^{7}Be, ^{124}Sb and ^{125}Sb [4]—[6].

The method applied at the ISTU operated at Kola NPP and upgraded to specifically remove ^{7}Be, ^{124}Sb, ^{125}Sb and other radionuclides was considered as a basic EC treatment approach for NVNPP-2 and LNPP-2 [4].

Experimental section

Equipment used and research methods

To determine the chemical composition of the EC, atomic absorption spectrometry, flame photometry and ion chromatography methods were applied. Its radionuclide composition was measured via α-, β- and γ-spectrometry. The radionuclide composition of the samples was measured using a GEM-15280-P-Plus ORTEC gamma spectrometer with a semiconductor HPGe detector. Total specific α- and β-activities were measured via an alpha-beta radiation radiometer with a highly sensitive 10-channel LB-770-2 counter. An OzO 10 series ozonizer with a rated ozone output of 10 g/h was used for ozonation.

Study of destructive EC processing methods

EC was **ozonated** with an oxygen-ozone mixture in a one-liter graduated cylinder placed in a thermostat. A porous stainless-steel plate was used as a gas distributor. The study was conducted in cycles at a temperature of 60 °C and at a pH level of ~ 12.

The precipitate formed during ozonation was separated using various filters:

- "white ribbon";
- "blue ribbon";
- porous stainless steel (PSS) with a TiO_2 coating and a pore size of 0.07 μm;
- PSS with a TiO_2 coating and a pore size of 0.2 μm.

The filtrate was measured by gamma spectrometry. The completeness of the filtrate oxidation process was monitored based on the measured chemical oxygen demand (COD).

EC **peroxidation** was studied as follows: concentrated HNO_3 was added to a 100 ml sample to a pH of 3. Then, 0.5 ml of a 10 g/L $FeSO_4$ solution were added. The sample was heated to 70—80 °C and hydrogen peroxide (at a concentration of 40 %) was added along with stirring performed until constant optical density could be achieved in the filtrate, the pH level was also monitored and adjusted along the way. The oxidized EC was passed through a double

"blue ribbon" filter and the resulting filtrate was analyzed via gamma spectrometry.

Study of sorption methods for EC processing

Under the study, 0.1 g of sorbent was added to 10 ml of EC, then stirred in sealed tubes for 2—7 days and passed through a double "blue ribbon" filter. Then, the filtrate was analyzed via gamma spectrometry.

To test selective sorbents under dynamic conditions, pre-oxidized EC was poured into a laboratory setup and pumped through four sequentially connected filters, each with a useful capacity of 7.5 ml filled with ferrocyanide sorbent. The EC was fed via a peristaltic pump at a flow rate of 60—65 ml/h. Samples were collected at the outlets of the second and fourth filter. The solution temperature accounted for 20—23 °C.

The following parameters were monitored:

- radionuclide composition of the initial solution and filtrates at the outlets of the second and fourth filter;
- total volume of the filtered solution;
- flow rate of solutions (periodic chronometry).

Study of radionuclide coprecipitation in EC

Radionuclide coprecipitation in EC was implemented using ferric chloride as collector due to its low cost and high efficiency in treating multiple radionuclides in alkaline and acidic environments. An aliquot (1—10 ml) of $FeCl_3$ (10 g/L) was added to 100 ml of EC, the pH level was adjusted to a desired one required for ferric chloride precipitation and the mixture was stirred with a magnetic stirrer for 15 minutes. The filtrate was analyzed via gamma spectrometry.

Results and discussion

Assessment of EC characteristics

The following radionuclides basically contribute to the radionuclide composition of the NVNPP-2 EC: ^{7}Be, ^{124,125}Sb, ^{137,134}Cs, ^{60}Co and ^{54}Mn. The specific activity of the most important radionuclides, namely, ^{124,125}Sb and ^{137,134}Cs, accounts for $n \times (10^3–10^4)$ Bq/L, pH > 12 (Table 1).

The radionuclide composition of the LNPP-2 EC is similar to that of the NVNPP-2 EC (Table 2), but is characterized by higher specific activity levels (^{124,125}Sb and ^{137,134}Cs — $n \times 10^5$ Bq/L).

According to its chemical composition, the NVNPP-2 EC is characterized by a salt content of approximately 150 g/L, which is primarily due to nitrates, borates and sodium carbonates. Due to the high pH level, the concentration of borates (calculated as boric acid) exceeds 50 g/dm^3 (Table 3).

Given planned pH adjustment of the NVNPP-2 EC to an acidic level, tetraborates present in an alkaline environment will convert to boric acid, the solubility of which is much lower than that of borates in an alkaline environment. The pH level adjustment my contribute to boric acid precipitate formation, which was confirmed during an experiment with the NVNPP-2 EC at a pH level of 3. To eliminate this negative effect, experiments were conducted: before pH adjustment, the EC was diluted with distilled water at a water/EC ratio of 0.1—0.5 in 0.1 increments. In further experiments, a water/EC ratio of 0.25/1 was adopted to prevent precipitate formation.

According to its chemical composition, the LNPP-2 and NVNPP-2 ECs are similar but the former is

Table 1. Radionuclide composition of NVNPP-2 EC

Sample No.	Sample ID	Sampling date	Specific activity, Bq/l						
			^{137}Cs	^{125}Sb	^{124}Sb	^{60}Co	^{134}Cs	^{54}Mn	^{7}Be
K1	20KPK30BB001	31.05.2024	8,500	65,800	16 500	1,640	700	712	700
K2	10KPK30BB002	31.05.2024	2,900	35,200	*	640	610	*	*
50	20KBF20AT001	23.09.2024	9,100	60,000	*	1,540	1,880	*	*
46	20KBF20AT001	29.10.2024	9,200	47,300	*	1,120	*	180	*

*below the detection threshold

Table 2. Radionuclide composition of LNPP-2 EC

Sample No.	Sample ID	Sampling date	Specific Activity, Bq/L			
			^{137}Cs	^{125}Sb	^{60}Co	^{134}Cs
143/2	20KPK20BB001	18.10.24	$1.9 \cdot 10^5$	$2.6 \cdot 10^5$	$6.4 \cdot 10^3$	$1.1 \cdot 10^5$
142/2	20KPK10BB001	16.10.24	$2.7 \cdot 10^5$	$3.44 \cdot 10^5$	$9.0 \cdot 10^3$	$1.59 \cdot 10^5$
144/1	20KPK10BB001	24.06.24	$2.09 \cdot 10^5$	$2.6 \cdot 10^5$	$7.0 \cdot 10^3$	$1.18 \cdot 10^5$
147/1	10KPK10BB002	24.06.24	$1.64 \cdot 10^5$	$7.7 \cdot 10^4$	$1.36 \cdot 10^4$	$3.6 \cdot 10^4$

Table 3. Chemical parameters of EC from NVNPP-2

Sample No.	Sample ID	Sampling date	pH	COD, mg/dm^3	Salt content, g/l
K1	20KPK30BB001	31.05.2024	>12	1,160	⩽150
K2	10KPK30BB002	31.05.2024	>12	1,930	
50	20KBF20AT001	23.09.2024	>12	820	
46	20KBF20AT001	29.10.2024	>12	1,010	

characterized by higher salt content (up to 400 g/L) and COD (up to 13.7 g/dm^3) which is explained by combined processing in the evaporators designed to treat floor drain and laundry waters, as well as lower pH (~ 10) (Table 4). No boric acid precipitation was observed in the LNPP-2 EC when the pH level was adjusted to the acidic one.

Table 4. Chemical parameters of EC from LNPP-2

Sample No.	Sample ID	Sampling date	pH	COD, mg/dm^3	Salt content, g/l
143/2	20KPK20BB001	18.10.24	10.1	13,700	376
142/2	20KPK10BB001	16.10.24	10.3	13,300	381
144/1	20KPK10BB001	24.06.24	10.2	12,100	286
147/1	10KPK10BB002	24.06.24	10.4	11,900	137

Findings from the ozonation process study

Ozonation was performed on four types of NVNPP-2 and LNPP-2 EC. Tables 5 and 6 present some examples of selected sample ozonation.

Table 5. Ozonation of EC from NVNPP-2, sample ID 20KPK30BB001 (No. K1) (V = 400 ml)

Time, min	pH	D^{400*}	O_2 flow rate, l/min	O_3 concentration, mg/l	Notes
90	>12	0.065	1.0	168	Foaming, defoamer was added, no sediment was formed
180	>12	0.036	1.0	164	No sediment, added collector – 10 ml $Co(NO_3)_2$ (5 g/l)
240	>12	0.030	1.0	171	Black sediment
360	>12	0.026	1.0	166	–
420	>12	0.027	1.0	170	Completion

*optical density of the sample at a wavelength of 400 nm

Table 6. Ozonation of EC from LNPP-2, sample ID 20KPK10BB001 (No. 142/2) (V = 400 ml, pH 10, adjusted to 12.16)

Time, min	pH	D^{400*}	O_2 flow rate, l/min	O_3 concentration, mg/l	Notes
90	9.99/12.1	0.249	1.0	167	Foaming, defoamer was added, pH adjusted upon completion
210	9.3/12.2	0.070	1.0	170	pH adjusted upon completion
330	10.4/12.2	0.030	1.0	172	Black sediment
450	12.0	0.031	1.0	171	Completion

*optical density of the sample at a wavelength of 400 nm

Table 7 summarizes data on the ozonation of NVNPP-2 and LNPP-2 EC.

Table 7. Summary data on EC ozonation

Sample No	COD init mgO_2/dm^3	COD fin O_2/dm^3	Collector introduction	Specific activity of filtrate*, Bq/dm^3 ^{60}Co/^{54}Mn	Concentration of suspended solids, g/dm^3
K1	1,160	0.058	+	< 20/< 20	0.098
K2	1,930	0.030	+	< 20/< 20	0.102
50	820	0.038	+	< 20/< 20	0.091
46	1,010	0.042	+	< 20/< 20	0.088
142/2	13, 700	0.045	–	< 20/< 20	1.51
143/2	13, 300	0.049	–	< 20/< 20	1.45
144/1	12, 100	0.034	–	< 20/< 20	1.30
147/1	11, 900	0.051	–	< 20/< 20	0.465

*minimum measurable specific activity

Tables 5—7 demonstrate that ozonation preceded by filtration on a double "blue ribbon" filter provides almost complete separation (to a specific activity of <20 Bq/L) of cobalt and manganese radionuclides. The concentration of suspended solids at the post-ozonation stage in the LNPP-2 EC appeared to be much higher than that of the NVNPP-2 EC, which is governed by the content of corrosion products in the original EC, such as iron, nickel and chromium, which are components of the structural stainless steel, as well as suspended solids entering the EC due to the processing of wastewater from the special laundry. Since the concentration of these components is much lower in the NVNPP-2 EC, no sediment is formed during ozonation.

Radionuclide coprecipitation was taking place on an additionally introduced collector of cobalt(II) nitrate at a concentration of 100 mg/L contributing to cobalt(+3) hydroxide generation upon ozonation. The concentration of suspended solids during

NVNPP-2 EC ozonation amounted to approximately 100 mg/L, which is an order of magnitude lower than that of the LNPP-2 EC.

Findings from the studied peroxide EC oxidation process

Peroxide EC oxidation was explored to determine its effectiveness as a destructive method proposed to destruct non-ionic forms of radionuclides, as well as its effect on subsequent sorption of radionuclides on inorganic sorbents.

The first peroxide oxidation experiments in an alkaline medium involving LNPP-2 EC (sample no. 142/2) showed that peroxide introduction contributed to abundant gas evolution indicating its self-decomposition. After adding 50 ml of peroxide per 100 ml of EC, the optical density of the filtrate in the collected sample decreased by only 1.5 times demonstrating the ineffectiveness of peroxide oxidation in an alkaline medium, which seems consistent with literature data [3]. Therefore, the process was subsequently carried out in an acidic medium.

Oxidation prompted water evaporation. The initial EC volume was maintained at a constant level: heated (distilled) water was added to it periodically and the temperature was maintained by a heating platform regulator. According to criteria set for the optical density of the filtrate, D^{400}, EC peroxidation could be judged as quite effective. Attempts to determine COD as a more accurate direct criterion yielded somewhat contradicting results. Apparently, excess hydrogen peroxide consumed at a high rate comparable to the initial EC volume interfered with obtaining somewhat reliable data.

At the post-peroxidation stage, the specific activity of ^{125}Sb in all EC filtrates dropped by 10—20%. However, it remained unchanged for the remaining radionuclides. All the resulting filtrates were used to determine K_d under static conditions using various sorbents. As subsequent sorption experiments under static and dynamic conditions showed, peroxidation cannot effectively remove ^{125}Sb from the EC.

Static sorption study of radionuclides in EC and its findings

Selective sorbents of the following grades produced on a pilot scale and supplied by JSC Inorganic Sorbents were applied in this study: T-35, T-3A, T-3K, T-3 and T-5, as well as sorbents from KB TEKHNAB OOO: LHT-9 (wt.%: TiO_2 — 80, N_2H_4 — 8, residue — water), LHT-M1 (wt.%: TiO_2 — 80, N_2H_4 — 8, Fe(CN) — 1—2, residue — water).

Tests were conducted on the original EC from NVNPP-2 and LNPP-2 in acidic and alkaline environments, as well as on EC previously subjected to ozonation and peroxide oxidation. Several conclusions can be drawn from the sorption experiments implemented under static conditions.

For NVNPP-2 EC:

- ^{125}Sb is poorly sorbed in an alkaline environment and K_d is no higher than 200;
- higher ^{125}Sb sorption is observed in an acidic environment at pH 3—5; even without oxidation, the K_d ranges from 2,000 to 3,000 for the T-35 sorbent and is even higher for the T-3 and T-5 sorbents;
- the best ^{125}Sb sorption efficiency was noted for the T-3 and T-5 sorbents;
- T-35 and LHT-M1 sorbents can be used to extract both ^{125}Sb and ^{137}Cs but the latter is mechanically unstable.

For LNPP-2 EC:

- ^{125}Sb sorption appears to be effective only in case of EC oxidized at pH 3. T-35 and LHT-M1 sorbents are capable of extracting both ^{125}Sb and ^{137}Cs but the latter is mechanically unstable and quickly wears away forming a turbid solution. Under dynamic conditions, this would lead to the breakthrough of small LHT-M1 particles into the filtrate and its contamination with radionuclides, which is unacceptable. Therefore, T-35 was chosen for further testing under dynamic conditions.

Study of radionuclide sorption under dynamic conditions and its findings

Sorption of radionuclides under dynamic conditions was implemented using the T-35 sorbent at pH 3. The EC from NVNPP-2 was studied provided its dilution with water at a water/EC ratio of 0.25. The EC from LNPP-2 was not diluted. The ozonation filtrate was pumped at a flow rate of 60 ml/h via a peristaltic pump through four 7.5 ml columns with sorbent having a height of approximately 30 cm. This value corresponds to a flow rate of four column volumes per hour and to the flow rate specified for EC treatment at the Kola and Smolensk NPP; i. e., the two columns corresponded in height to one DShAK filter container. Samples were periodically collected from the second and fourth columns and analyzed via gamma spectrometry.

The first experiment was performed on the initial NVNPP-2 EC (No. K1). ^{125}Sb extraction rate was low indicating the presence of its non-ionic forms. Furthermore, when the EC was fed through the T-35 sorbent after the pH adjustment, gas evolution was observed on its granules, which was caused by the prolonged decomposition of carbonates in the EC apparently reducing the effectiveness of its treatment from ^{125}Sb radionuclides. Therefore, subsequent tests were conducted on EC filtrates after oxidation and degassing at a temperature of ~ 60 °C and stirred for 1 hour.

Table 8 presents the results for the NVNPP-2 EC (No. K1) treatment at the post-ozonation and post-filtration stage, as well as the characteristics of the spent sorbent.

Table 8. Results of radionuclide sorption from NVNPP-2 EC, sample ID 20KPK30BB001 (No. K1) at the post-ozonation and post-filtration stage using T-35 sorbent.

Initial specific activity, Bq/L: ^{137}Cs – 8,600, ^{125}Sb – $4.5 \cdot 10^4$, ^{124}Sb – $1.02 \cdot 10^4$, pH ~ 3, v = 60 mL/h

№ col.	pH	Filtrate volume V, ml	c.v.*	Specific activity of filtrate, Bq/l		
				^{137}Cs	^{125}Sb	^{124}Sb
4	5.30	460	31	<15	<15	<15
2	–	560	37	<15	200	45
4	–	1,440	96	<15	190	68
2	–	1,540	103	<15	3,700	820
4	–	1,905	127	<15	480	75
2	–	2,005	134	<15	5,400	1,300
4	4.90	2,890	193	<15	870	200
2	–	2,990	199	<15	9,800	2,200
4	4.91	3,415	228	<15	1,300	300
2	–	3,465	231	<15	12,400	2,800
4	4.90	4,330	289	<15	2,100	500

*c.v. – column volume

As can be seen from Table 8, significant breakthrough of ^{125}Sb radionuclides occurs even after passing 100 c.v., which was confirmed by the analyzed specific activity of the spent sorbent. While cesium and beryllium isotopes are almost completely extracted in the first column, ^{124,125}Sb is distributed across all four. This indicates lower antimony sorption kinetics compared to cesium, so the flow rate of the EC through the T-35 was reduced to 2 c.v./h (30 ml/h). The treatment efficiency for radionuclides grew up slightly but nevertheless remained insufficient.

To address this issue, the LHT-M1 sorbent supplied by KB TEKHNAB OOO was tested for EC treatment (No. K1). However, the treatment efficiency of EC No. K1 using the KB TEKHNAB sorbent turned out even lower than the one observed in case of the T-35 sorbent.

Coming back to post-ozonation and post-filtration EC treatment, it should be noted that the pH of the solution after sorption on T-35 accounted for 4—5 with an initial pH of 3. Apparently, the pH affects in a great way the antimony sorption kinetics, so T-35 was converted to the H^+ form. Moreover, at our request, employees of JSC Inorganic Sorbents manufactured a pilot batch of this sorbent in the H^+ form.

At the post-ozonation and post-filtration stages, the NVNPP-2 EC (No. K2) was treated on T-35 sorbent converted to the H^+ form. Table 9 summarizes the treatment results.

Table 9. Results of post-ozonation and post-filtration radionuclide sorption from the NVNPP-2 EC, sample ID 10KRK30BB002 (No. K2) on T-35 sorbent in the H+ form.

Initial specific activity, Bq/L: ^{137}Cs – 1430, ^{125}Sb – $1.6 \cdot 10^4$, pH ~ 3.4 T-35 columns, v = 30 mL/h

Col. No.	pH	Filtrate volume V, ml	c.v.*	Specific activity of filtrate, Bq/L	
				^{137}Cs	^{125}Sb
4	2.50	247	16	<8	<8
4	2.26	702	47	17	51
2	–	782	52	<8	<8
4	2.30	982	65	19	<8
4	2.28	1,432	95	<8	<8
2	–	1,482	99	<8	<8
4	2.98	1,707	114	<8	<8
4	3.00	2,162	144	<8	<8
2	–	2,212	147	<8	<8
4	3.18	2,442	163	<8	<8
4	2.99	2,892	193	17	<8
2	–	2,957	197	<8	<8
4	3.04	3,147	210	<8	<8
4	3.09	3,492	233	<8	<8
4	3.05	3,692	246	<8	<8
2	3.53	3,752	250	<8	300
4	3.42	4,215	281	<8	<8
4	3.61	4,875	325	<8	<8
2	3.82	4,935	329	<8	1,500
4	3.78	5,625	375	<8	<8
4	3.92	6,030	402	<8	120
2	4.12	6,090	406	25	5,300
4	4.25	6,555	437	<8	930
4	4.24	6,930	462	22	2,700

*c.v. – column volume

The specific activity of the combined filtrate, Bq/dm^3, was as follows: ^{125}Sb — 170, ^{60}Co < 1.3, ^{22}Na — 17, ^{137}Cs — 6.5; specific activity of dry salts, Bq/kg: Sb — 1,100, ^{60}Co < 110, ^{22}Na — 440, ^{137}Cs — 40.

As can be seen, treatment of NNPP-2 EC (No. K2) based on such methods as ozonation, filtration and sorption on T-35 in the H+ form generates both a solution and salts that are not referred to the RW category. Moreover, the sorbent capacity exceeded 400 c.v.

At the post-ozonation and post-filtration stage, LNPP-2 EC (No. 142/2) was treated on T-35 sorbent converted to the H^+ form. This sample was selected for testing as it had the highest specific activity for cesium and antimony radionuclides and the highest COD. Table 10 summarizes the treatment results.

Table 10. Results of post-ozonation and post-filtration radionuclide sorption from the LNPP-2 EC, sample ID 20KRK10BB001 (No. 142/2), on T-35 sorbent (converted to the H^+ form).

Initial specific activity, Bq/L: ^{137}Cs – $2.16 \cdot 10^5$, ^{125}Sb – $2.6 \cdot 10^5$, pH ~ 3, v = 30 mL/h

Col. No.	pH	Filtrate volume V, ml	C.V.	Specific activity of filtrate, Bq/L	
				^{137}Cs	^{125}Sb
4	2.45	218	15	<4	<13
4	2.89	678	45	<4	<13
2	–	733	49	<4	52
4	3.01	968	65	<4	<13
4	3.08	1,413	94	<4	<13
2	–	1,463	98	<4	63
4	2.80	1,688	113	<4	23
4	3.10	2,148	143	<4	<13
2	–	2,198	147	<4	215
4	3.11	2,438	167	<4	<13
4	2.85	2,888	193	<4	150
2	–	2,943	196	<4	560
4	2.96	3,138	209	<4	140
4	3.14	3,343	223	<4	155
2	3.67	3,405	227	<4	1,350
4	3.52	3,885	259	<4	165
4	3.61	4,320	288	<4	160
2	3.78	4,380	292	<4	19,000
4	4.08	4,815	321	<4	1,700
4	4.21	5,445	363	<4	24,000

The specific activity of the combined filtrate was as follows, Bq/dm^3: ^{125}Sb — 2,000, ^{60}Co < 3.1, ^{40}K — 1,700, ^{75}Se — 67, ^{22}Na — 27, ^{137}Cs < 3.8, and for dry salts, Bq/kg: Sb — 5,200, ^{60}Co < 110, ^{40}K — 4,200, ^{75}Se — 110. As can be seen, the specific activity of both the filtrate and dry salts depends on the content of the natural isotope ^{40}K, i. e. the use of ozonation, filtration and sorption on T-35 in the H^+ form in treating the LNPP-2 EC generates solution and salts that are not referred to the RW category. Moreover, the sorbent resource exceeded 300 c.v.

Thus, the tests revealed a method based on which the main radionuclides could be removed from the NVNPP-2 and LNPP-2 EC. This method involves ozonation, filtration to separate the precipitate formed during ozonation, pH adjustment with degassing (carbonate removal) and sorption on T-35 converted to the H^+ form at a pH of 3.

Study of radionuclide coprecipitation in EC and its results

Out of the precipitation methods, coprecipitation on iron hydroxide appears preferable as it is able to collect a large radionuclide inventory, including ^{7}Be, ^{124}Sb and ^{125}Sb. Experiments have shown that this method is much more effective in an acidic environment, but still is not able to treat NVNPP-2 and LNPP-2 EC from antimony to the required levels. Furthermore, it generates large secondary waste volumes, which contradicts the low-waste principle.

Filtration ranking

The sediment generated from the NVNPP-2 and LNPP-2 EC ozonation was separated using filters with pore sizes of 10—20 μm (“white ribbon”), 1—2 μm (“blue ribbon”), 200 nm (PNS), and 7 nm (PNS).

Tables 11 and 12 summarizes data on the analyzed solutions obtained after ozonation and filtration on various filters.

Table 11. Summary data on radionuclide removal from LNPP-2 EC, sample ID 20KPK10BB001 (No. 142/2), through ozonation and subsequent sediment separation using various filters.

Initial specific activity of wastewater, Bq/L: ^{60}Co – $1.2 \cdot 10^4$, ^{54}Mn – 880

Filter brand, pore size, μm	“White ribbon”, ~10—20	“Blue ribbon”, ~1—2	PNS, 0.2	PNS, 0.007
Specific activity of filtrate by ^{60}Co/^{54}Mn, Bq/kg	530/< 20	60/< 20	<20/< 20	< 20/< 20

Table 12. Summary data on radionuclide removal from the NVNPP-2 EC, sample ID 20KPK30BB001 (No. K1), through ozonation and subsequent sediment separation using various filters.

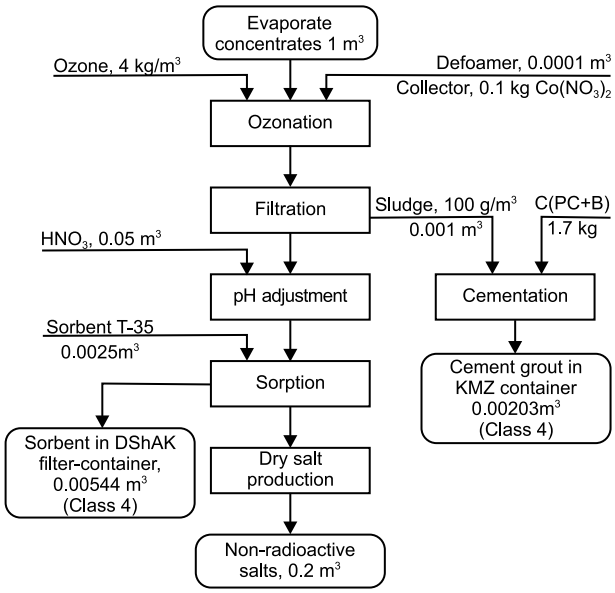
Initial specific activity, Bq/L: ^{60}Co – 1,640, ^{54}Mn – 712

Filter brand, pore size, μm	“White ribbon”, ~10—20	“Blue ribbon”, ~1—2	PNS, 0.2	PNS, 0.007
Specific activity of filtrate by ^{60}Co/^{54}Mn, Bq/kg	230/< 20	50/< 20	< 20/< 20	< 20/< 20

As can be seen from these tables, the use of a filter membrane with a pore size of 0.2 μm ensures the separation of the sediment along with ^{60}Co and ^{54}Mn to a level below the minimum detectable specific activity.

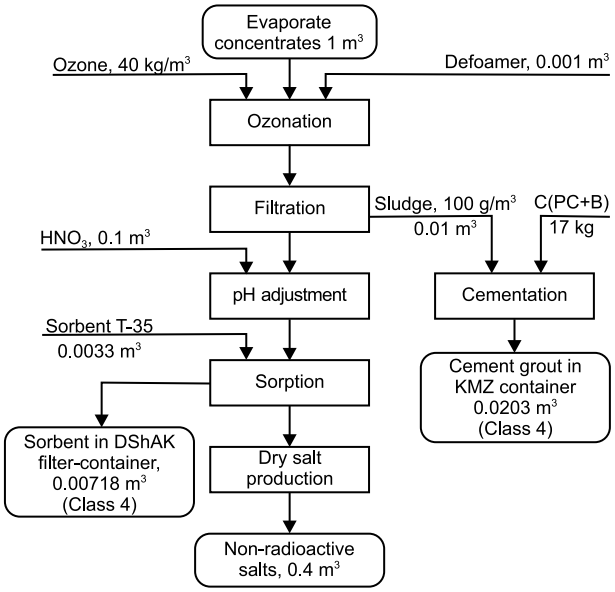
Material balance

Based on the above, a preliminary material balance of the developed flowchart was compiled based on the case studies of the NVNPP-2 (Fig. 1) and LNPP-2 EC (Fig. 2) treatment. The following initial data was used to calculate the material balance for NVNPP-2 EC processing:



V_{tot} = 0.00544 + 0.00203 = 0.00747 m³; VRF =132

Fig. 1. Preliminary material balance for the NVNPP-2 EC treatment



$V_{RW} = V_c + V_{cR}$ = 0.00718 + 0.02748 = 0.00747 m³; VRF =36.4

Fig. 2. Preliminary material balance for the LNPP-2 EC treatment

- Treated volume — 1 m³;
- O_3 consumption, kg (COD×3)×1.2=1×3×1.2=4 kg/m³;
- Defoamer consumption, m³ — 0.001 (not accounted for);
- Collector consumption, kg — 0.1 (not accounted for);
- Nitric acid consumption, m³ — 0.05 (or 65 kg);
- T-35 consumption, 1/400, m³ — 0.0025 (based on the experiments, sorbent capacity was assumed as being equal to 400 c.v.).

Initial data used to calculate the material balance in case of LNPP-2 EC processing:

- Treated volume —1 m³;
- O_3 consumption, kg (COD×3)×1.2=10×3×1.2=40 kg/m³;
- Defoamer consumption, m³×0.001 (not accounted for);
- Collector consumption, kg — 0.1 (not accounted for);
- Nitric acid consumption, m³ — 0.1 (or 130 kg);
- T-35 consumption, 1/300, m³ — 0.0033 (based on the experiments, sorbent capacity was assumed as being equal to 300 c.v.).

To calculate the material balance, taking into account the containers used to store and condition the RW the following conditions were assumed.

EC treatment via ozonation will generate 0.1 kg of sludge (sediment) per 1 m³ of treated EC and when concentrated to 100 kg/m³ — 0.1×1/100=0.001 m³. Thickened sludge cementation will involve 0.0017 m³ of cement mortar.

The cement compound resulting from sludge hardening is emplaced into KMZ-type containers. In this case, the volume of RW subject to disposal grows by a ratio of 3.7/3.1, where 3.7 and 3.1 m³ are the total and useful capacities of the container, respectively.

A 120-liter sorbent is contained in a filter container with a diameter of 4.7 dm and a height of 7.05 dm. Based on the performed experiments, we assume the specific activity of the spent sorbent to be equal to 108 Bq/kg for both ^{137}Cs and ^{125}Sb. Given such specific activity levels, to provide the required biological shielding the filter container should be 5 cm thick and made of carbon steel (AEDR 0.1 m, mSv/h < 2), its external volume will account for 205 liters, and given the geometry, it will grow by 205 liters/(120 liters×0.785)=2.17 times.

Table 13 summarize the material balance calculations.

Table 13. Volume of secondary waste per 1 m³ of waste and volume reduction factors (VRF) of waste calculated for NVNPP-2 and LNPP-2

Parameter	NVNPP-2	LNPP-2
Sorbent volume, m³	0.0025	0.0033
Volume of containerized sorbent, m³	0.00544	0.00718
Volume of cemented sludge, m³	0.0017	0.017
Volume of containerized compound with sludge, m³	0.00203	0.0203
Total volume of secondary waste, m³	0.00754	0.0275
VRF relative to evaporator concentrate*	132.6	36.4
VRF relative to initial LRW*	3,900	3,270

Conclusion

1. Based on literature data and analyzed sorbent brands, a range of selective sorption materials considered most promising for the extraction of the main dose-contributing radionuclides from EC was identified.

2. Chemical and radionuclide compositions of EC from the NNPP-2 and LNPP-2 were identified. Their specific activity is primarily contributed by such radionuclides as ^{7}Be, ^{124,125}Sb, ^{137,134}Cs, ^{60}Co and ^{54}Mn; the activity of the most important ones, i. e., ^{124,125}Sb and ^{137,134}Cs, accounts for n×10^{5} Bq/L. The salt content in the EC amounts to 150—400 g/L at a pH of 10—12, which is mainly due to the presence of sodium nitrates, borates and carbonates.

3. Distribution K_d and treatment K_{tr} coefficients were calculated for radionuclides present in the NVNPP-2 and LNPP-2 EC under static conditions in alkaline and acidic environments provided the use of selected selective sorption materials considering the following cases — no treatment, after ozonation and peroxide oxidation. T-35 and LHT-M1 sorbents are capable of extracting both ^{125}Sb and ^{137}Cs but the latter one is mechanically unstable. Antimony sorption is effective only in case of oxidized EC at pH 3.

4. Ozonation was chosen as the primary destructive method to convert non-ionic forms of EC radionuclides into ionic ones. It was found that a filter membrane with a pore size of 0.2 μm may provide reliable separation of the precipitate generated during EC ozonation along with ^{60}Co, ^{54}Mn and other contaminants.

5. Treatment coefficients were calculated for co-precipitation of radionuclides in EC using iron hydroxide in an acidic medium. It was found that this method cannot provide the required levels of antimony removal from NVNPP-2 and LNPP-2 EC.

6. Based on sorption studies performed under dynamic conditions, a process flowsheet can be proposed for NVNPP-2 and LNPP-2 EC treatment from radionuclides involving such stages as ozonation, filtration, pH level adjustment to 3 with degassing and sorption on T-35 in the H^+ form at pH 3. The sorbent resource for the NVNPP-2 and LNPP-2 EC accounted for 400 c.v. and 300 c.v. respectively. The RW volume reduction factor calculated based on the preliminary material balance was equal to 132.6 and 36.4 for the NVNPP-2 and LNPP-2 EC respectively. The RW volume reduction factor was recalculated considering EC treatment per unit volume of the original LRS. It amounted to ~ 3,900 and 3,270 for the NVNPP-2 and LNPP-2 EC respectively.

References

1. Povarov V. P., Gusev I. N., Rosnovsky S. V. et al. Opyt vnedreniya sistem ionoselektivnoy ochistki trapnykh vod ot radionuklidov na blokakh 1—2 NVAS-2 [Experience in implementation of systems applied for drainage water ion-selective purification from radionuclides at units 1,2 of Novovoronezh-2 NPP]. *ANRI — ANRY Journal,* 2020, no. 4 (103), pp. 64—70. DOI: 10.37414/2075-1338-2020-103-4-64-70.

2. Savkin A. E. *Pererabotka kubovykh ostatkov AES s ispol'zovaniyem selektivnykh sorbentov* [Processing of NPP Still Bottoms by Selective Sorbents]. Abstract of a PhD Dissertation]. Moscow, 1999. 24 p.

3. Savkin A. E., Morenova A. G., Zakharova E. V., Rodygina N. I. Okislitel'no- sorbtsionnaya ochistka kubovykh ostatkov Leningradskoy AES ot radionuklidov [Oxidation-Sorption Removal of Radionuclides from Still Bottoms at the Leningrad NPP]. *Radiokhimiya — Radiochemistry,* 2003, vol. 45, no. 4, pp. 362—370.

4. Avezniyazov S. R., Stakhiv M. R. Opyt raboty po obrashcheniyu s ZHRO na Kol'skoy AES [Experience of recycling the liquid radioactive waste at the Kola NPP]. *Radioaktivnyye otkhody — Radioactive Waste,* 2018, no. 4 (5), pp. 49—54.

5. Sharygin L. M. *Termostoykiye neorganicheskiye sorbenty* [Heat-Resistant Inorganic Sorbents]. Yekaterinburg, Ural Branch of the Russian Academy of Sciences Publ., 2012. 303 p.

6. Tusa E. H. IVO's nuclide removal system takes to the road. *Nucl. Eng. Int.,* 1995, vol. 40, no. 492, pp. 41—42.

7. Nikiforov A. S., Kulichenko V. V., Zhikharev M. I. *Obezvrezhivaniye zhidkikh radioaktivnykh otkhodov* [Neutralization of liquid radioactive waste]. Moscow, Energoatomizdat Publ., 1985. 184 p.

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