Application of the Sorption-Membrane Technologies for Liquid Radioactive Waste Processing at Kursk NPP

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ABSTRACT

Experimental tests of the technology for NPP wastewater processing were conducted in the beginning of 2005. Wastewater effluents contained anion-active surface-active substances (SAS) in the concentration of 5-10 mg/L; total salt bearing of the effluents was about 0.8 g/L; specific activity of the ^{95}Zr, ^{95}Nb, ^{60}Co, ^{59}Fe, ^{54}Mn, ^{51}Cr, and ^{137}Cs was within the range of 50-200 Bq/L; gross specific activity amounted 700-800 Bq/L.

The experimental facility for wastewater processing consists of the following modules and units:

- ozonizing module;
- microfiltration module based on a cross-flow filtering unit equipped with the metal-ceramic Trumem membranes;
- sorption end-polishing unit loaded with the cesium-selective sorbent and conventional cation and anion exchange resins.

After all SAS and other organic contaminants were destroyed at the ozonizing stage, all radionuclides except ^{137}Cs were retained at the microfiltration stage. The end-polishing selective sorption unit provided further removal of ^{137}Cs radionuclide to the level of 2-3 Bq/L.
Total volume of various wastewater effluents processed at the experimental facility amounted 670 L. The volume of the secondary waste concentrate was 0.3% of the feed, i.e. the waste concentrating factor reached 350.

INTRODUCTION

In the process of the nuclear power plant (NPP) operation considerable quantities of liquid radioactive waste (LRW) are generated, the processing of those being rather important and complicated issue.

Today in Russia evaporation is used to treat LRW from nuclear power plants [1]. The resulting salt slurry is transferred into special tanks for the long-term storage. This method of LRW processing has straightforward technology, simple engineering embodiment and fits easily into the NPP operation cycle. However, inherent disadvantages of the process, such as high foaming from surface-active substances in LRW and the large volume of salt residue present considerable technical difficulties both for the operation, storage and further processing of the waste [2].

We have developed a new technology based on the principle of the successive decontamination of LRW from the following species present in it:

- organic compounds (surface-active substances (SAS), complexing agents, petroleum products, etc.) – by means of the ozonizing technique;
- radionuclides in the form of suspended and/or colloidal particles – by means of the microfiltration technique;
- radionuclides in the ionic form – by means of the sorption technique.

This paper reports the results of semi-full scale tests of the technology for processing the laundry waste, one of the LRW types formed at nuclear power plants in large quantities.

TEST PROCEDURES AND TECHNIQUES

To demonstrate the technology developed for the laundry waste processing an experimental facility has been designed and constructed. The facility consists of three main units as follows: the ozonizing unit, the microfiltration unit, and the sorption unit. Description of the design and principle of the unit operation are given below in more detail.

Tests of the experimental facility were conducted in the period of April through August 2005 with the actual special laundry water of Kursk NPP. During the tests the following parameters of the wastewater effluent were determined: pH, the total salt bearing, COD (Chemical Oxygen Demand), the concentration of anion-active surface-active substances (ASAS), the ammonia concentration, and the specific activity of gamma-emitting radionuclides.

Chemical and radionuclide composition of the special laundry water is given in Tables I and II, respectively.

Table I. Chemical Composition of the Special Laundry Wastewater at Kursk NPP

Parameter value	pH	COD, mgO/L	ASAS concentration, mg/L	Salt bearing, g/L	Ammonia concentration, mg/L
minimum-maximum value	6.8-8.3	10-21	2.1-12.5	0.39-1.34	12- 43
average value, confidence interval	7.4±0.5	16±5	5.7±3.2	0.74±0.21	25±11

Table II. Radionuclide Composition of the Special Laundry Water at Kursk NPP

Parameter value	Specific activity of radionuclides in water, Bq/L							
	^{95}Zr+ ^{95}Nb	^{60}Co	^{59}Fe	^{54}Mn	^{51}Cr	^{134}Cs	^{137}Cs	gross gamma-emitters
Minimum-maximum value	10-700	11-790	3-560	9-530	3-720	3-55	10-140	80-2780
average value	250	170	80	120	230	10	55	910

The data shown in Tables I and II indicate that the special laundry water belongs to the low-level LRW, values of chemical and radioactive component composition ranging widely.

Tests of the ozonizing unit

Special laundry water was ozonized to remove SAS and other organic compound contaminants by means of chemically destructing thereof with the ozone gas.

The process of water ozonizing was conducted as follows. A 50-90 L portion of the feed laundry wastewater was loaded into the stainless steel reactor vessel of 110 L operating volume and the circulating pump was started. Wastewater was circulated through the high performance ejection mixer where it was mixed with the ozone-oxygen gas coming from the ozonizer. The ozonizer output was 7 g of the ozone gas per hour, and the oxygen flow through the ozonizer was set to maintain the 100 mg/L concentration of the ozone in the gas mix. The circulating solution was sampled periodically and analyzed for the ASAS content. Exhausted gaseous phase passed successively through the foam separating trap, through the ozone catcher loaded with the ozone destruction catalyst, and was released into the atmosphere.

In Table III the effect of the ozonizing time on the ASAS concentration for different batches of the special laundry wastewater is given.

Table III. The Dependence of ASAS Concentration on the Ozonizing Time for Different Batches of the Special Laundry Wastewater

Ozonizing time, hr	ASAS concentration in wastewater, mg/L					
	Batch No.5 (50L volume)	Batch No.6 (50L volume)	Batch No.7 (75L volume)	Batch No.8 (90L volume)	Batch No.9 (90L volume)	Batch No.10 (90 L volume)
0	4.2	5.5	2.8	12.5	11.0	6.3
1	1.3	1.2	0.2	4.4	2.3	3.1
2	0.5	0.4	< 0.1	1.6	0.64	1.5
3	-	0.2	-	0.5	0.35	0.6
4	-	-	-	-	0.2	-

Results given in Table III show that 2-3 hours of ozonizing time is enough for practically complete ASAS destruction. Gross ozone gas consumption to reduce the ASAS concentration below 1 mg/L is 10-12 g per 1 g of ASAS.

In Table IV chemical composition of the laundry wastewater after the ozonizing stage is given. Results obtained show the pH and salt bearing values remain practically the same and the COD value to be reduced below the instrumental detection limit (10 mg O/L). Ammonia concentration in water is also reduced by a factor of 2-3 as a result of the ozonizing.

Thus, tests of the ozonizing unit proved its high destruction performance for ASAS present in special laundry wastewater and for partial removal of ammonia as well.

Table IV. Chemical Composition of the Special Laundry Wastewater after the Ozonizing Stage

Parameter value	pH	COD, mgO/L	ASAS concentration, mg/L	Salt bearing, g/L	Ammonia concentration, mg/L мг/л
minimum/ maximum value	7.2-8.5	<10	0.1-0.6	0.28-0.95	8-15

Tests of the microfiltration unit

Microfiltration unit is used for removing radionuclides present in wastewater as suspended and colloidal species by means of filtering the solution through the microfiltration membrane.

Our unit was equipped with the Trumem™ metal-ceramic membranes with the pore size of 0.2 μm and the total filtering area of about 0.2 m^2.

Tests were conducted as follows: wastewater after the ozonizing stage was fed into the circulation loop of the microfiltration unit by a peristaltic pump. The block of filtering membrane pockets separated the wastewater flow into two streams: permeate and concentrate. Permeate of the microfiltration stage was collected into the permeate tank and analyzed for the presence of gamma-emitters. The starting filtration flow rate in the tests amounted 25-30 L/hr or 125-150 $L/m^2/hr$. As the suspended particle concentration in the loop increased, the filtration flow rate gradually decreased. After the filtration flow rate gets below 10 L/hr (50 $L/m^2/hr$) the process was shut down, the concentrate from the circulation loop was removed and collected in a separate vessel, and the block of filtering membrane pockets was backwashed with water.

Values of the specific gamma activity of the microfiltration permeate for different processed wastewater batches are summarized in Table V.

Table V. Radionuclide Composition of the Special Laundry Wastewater after the Ozonizing and Microfiltration Stages

Parameter value	Specific activity of radionuclides in wastewater, Bq/L							
	^{95}Zr+ ^{95}Nb	^{60}Co	^{59}Fe	^{54}Mn	^{51}Cr	^{137}Cs	^{134}Cs	Gross gamma-emitters
minimum/ maximum value	<3	<3	<3	3-7	3-40	15-40	3-11	15-90

Results given in Table V show that the application of Trumem™ membranes allows the decontamination of the special laundry wastewater from the majority of the radionuclides present to the detection limit of the instrumentation equipment used (below 3 Bq/L). The breakthrough observed for ^{51}Cr and ^{137}Cs radionuclides was stipulated by the ionic speciation of those radionuclides in water. The chemical wastewater composition during the microfiltration stage remains intact.

Further decontamination of the wastewater flow, primarily from the long-lived ^{137}Cs radionuclide was performed on the sorption end-polishing stage.

Tests of the sorption end-polishing unit

The sorption end-polishing unit consists of three stainless steel columns connected in series. The columns are loaded with the selective ferrocyanide FNS sorbent (TU 2161-002-51255813-2005), KU-2x8 sulfocationite, and AV-17x8 anionite respectively. Operating volume of the sorbent bed is about 1 L in each column.

Taking into account the residual wastewater contamination by ^{137}Cs the sorption end-polishing was conducted using merely the FNS sorbent possessing high selectivity towards cesium [3]. Permeate from the microfiltration unit was passed through the FNS-loaded column, and the emerging filtrate was collected in the receiving tank and analyzed for the specific activity of gamma-emitters. The filtration flow rate at the sorption stage during the tests was 7-10 L/hr. The results obtained for all feed batches showed the specific activity in the filtrate for all the radionuclides determined to be not higher than 3 Bq/L, the value of the detection limit for the instrumentation equipment used.

RESULTS AND DISCUSSION

In Table VI characteristics of the feed and decontaminated special laundry wastewater of Kursk NPP are given.

Table VI. Characteristics of the Feed and Decontaminated Special Laundry Wastewater of Kursk NPP

##	Parameter	Unit of measure	Parameter value	
			feed	decontaminated water
1	Organoleptic properties	-	Opaque, foamy, smelly liquid, off-gray in color	Transparent, colorless, odorless liquid
2	pH	-	7-8	7-8
3	Salt bearing	g/L	0.6-1.2	0.6-1.2
4	COD	mg O/L	10-20	<10
5	ASAS concentration	mg/L	5-12	0.1-0.2
6	Specific activity of ^{95}Zr- ^{95}Nb, ^{60}Co, ^{59}Fe, ^{54}Mn, and ^{137}Cs radionuclides	Bq/L	10-800	< 3

Results given in Table VI show that the application of ozonizing, microfiltration, and sorption processes allow the special laundry wastewater decontamination from chemical and radioactive impurities to the norms permitting the release of water into an industrial sewer.

In the tests several wastewater batches of the total quantity of about 850 L have been processed. About 2 L of the concentrate has been obtained. The concentrate was a suspension of 60 g/L solids and the gross gamma-activity of $2.5 \cdot 10^5$ Bq/L or $4.0 \cdot 10^6$ Bq/kg (counting by the solid phase). The secondary waste volume (the concentrate volume) amounted 0.23% of the feed wastewater volume, in other words, the waste volume reduction/concentrating factor was about 420.

The secondary waste obtained according to the technology is a suspension of hydroxides and carbonates of iron, chromium, nickel, calcium, magnesium and other metals with radionuclides

strongly adsorbed on the suspended solids. After partial and/or complete dewatering the secondary waste could be solidified according to a conventional technique, for example, by cementation. In the latter case the gross waste volume reduction/concentrating factor could reach as high as 4000.
Thus, semi-full scale tests of the developed technology demonstrated its high performance in decontaminating special laundry wastewater from surface active substances and from all the radionuclides present in it. The decontamination factor of the feed from the above mentioned impurities was above 99%, which allowed release of the decontaminated water into the common sewer without an evaporation stage. The final solidified secondary waste volume according to the developed technology is 30-40 times less as compared to the standard solidification of evaporator concentrates.

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