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## **PURIFICATION OF DRAIN WATER AND DISTILLATION RESIDUE FROM ORGANIC COMPOUNDS, TRANSURANIC ELEMENTS, AND URANIUM AT THE CHORNOBYL NPP**



*The research deals with the purification of drain water and distillation residue from organic (polymeric) compounds, transuranic elements, and uranium. The pretreatment method with the use of Sizol type coagulant-flocculant and catalytic oxidation with hydrogen peroxide and ultrafiltration has been proposed. This method prevents the evaporator coking by dust-suppressor and other organic substances vulcanized by heating. The removal of alpha-emitting radionuclides results in the increasing safety of the nuclear power plant operation.*

*Key words: drain water, distillation residue, the Chornobyl nuclear power plant, organic compounds, transuranic elements, and uranium.*

The problem of liquid radioactive waste (LRW) is highly relevant for the Chornobyl NPP. At the Chornobyl NPP, the scheme for LRW treatment is optimized in accordance with the Joint Convention on the Safety of Spent Waste Management and on the Safety of Radioactive Waste Management. Thanks to the assistance of the International Atomic Energy Agency (IAEA), at the Chornobyl NPP, there has been established a pilot plant to address the problem of LRW primary treatment from organic polymeric compounds and transuranic elements (TRU) for subsequent processing at the existing facilities of Chornobyl NPP chemical plant or at the LRW retreatment plant that is under construction now. Currently, over 20 000 m<sup>3</sup> of liquid radioactive waste residue have been accumulated at the Chornobyl NPP. The auxiliary evaporators located at the chemical plant and at

the LRW treatment plant are designed in different ways: at the chemical plant the auxiliary evaporator can be repaired by cleaning its interior surface from the cured polymer deposits, whereas at the newly built plant the design of auxiliary evaporator does not provide for any similar repair.

The repair works can result in the suspension of process flows. The interaction of man-made and natural waters with fuel-containing materials at the *Shelter* facility of Chornobyl NPP leads to the formation of radioactive water. The *Shelter* facility is a complex of protective structures over the inactive 4<sup>th</sup> reactor destroyed by the man-made disaster. The *Shelter's* water contain gamma-, beta-, and alpha-emitters, including Pu, Am, Cm, U, and other radionuclides. In addition, they bear the components of dust-suppressive emulsion used at the *Shelter* facility, namely, a polymeric compound OP-7 (a siloxane-acrylate binder and a nonionic surfactant), glycerol, oxalic, oleic, and oxyethylenediphosphonic acids, as well

as ethyl alcohol. This radioactive water falls into the special drainage system of the 3<sup>rd</sup> reactor main building where it is mixed with drain water. Further, as the mixed water accumulates, it is transported to the facilities of Chornobyl NPP for being evaporated to the maximum salt concentration. The concentration of organic compounds in these water is 0.4–0.6 g/dm<sup>3</sup>, while dichromate oxidation factor (COD, chemical oxygen demand index) reaches 2000–3500 mg O<sub>2</sub>/dm<sup>3</sup>. For further treatment of LRW by evaporation the content of organic matter in radioactive water should be reduced to COD ≤ 200 mg O<sub>2</sub>/dm<sup>3</sup>, whereas the volumetric activity of alpha emitters should be at the level of ≤ 370 Bq/dm<sup>3</sup>.

The world practice lacks in experience in treating LRW arising from man-made nuclear accident. There exists a method for oxidative purification of LRW distillation residue at the Leningrad NPP hydrogen by peroxide and potassium permanganate to reduce the content of organic compounds [1]. The ferrocyanide sorbent is used to reduce the activity of radionuclides <sup>134</sup>Cs, <sup>137</sup>Cs and <sup>60</sup>Co. For more complex systems containing many various organic (polymeric) compounds and a significant amount of alpha-emitting nuclides, no data on effective ways to reduce the content of organic matter and TUE have been available.

As part of work on LRW treatment, the studies have been carried out to prove promising application of coagulation, catalytic oxidation by hydrogen peroxide, and membrane technique for removal of organic compounds and radionuclides.

The advantages of coagulation method are as follows:

1) Low cost of cleaning; 2) simplicity of the equipment used; 3) possibility to remove organic substances and radionuclides in ionic and colloidal phases; 4) saline waste treatment option [2].

### THE EXPERIMENT

The activity of gamma-emitting nuclides <sup>137</sup>Cs and <sup>241</sup>Am was measured on gamma-spectrometric complex consisting of a fine germanium semi-

conductor detector GL2020R manufactured by *CANBERRA* with a resolution of 0.57 keV for gamma rays energy of 122 keV (<sup>57</sup>Co gamma line) and a *CANBERRA* 16 000-channel pulse-height analyzer. The full scale covers the range from 10 to 1400 keV. The detector has a 500-micron thick beryllium window. The minimum measurable activity for the measurement geometry on gamma line of 59 keV is equal to 0.03 Bq/sample for <sup>241</sup>Am, and 0.4 Bq/sample for <sup>137</sup>Cs (661.6 keV). The instrumental spectra were processed using the GENIE-2000 program by the algorithms contained in the program.

<sup>90</sup>Sr was separated by the extraction chromatographic method. The PTFE 4 powder impregnated with a solution of 0.4 mol/dm<sup>3</sup> ether dicyclohexyl-18-crown-6 in chloroform was used as carrier. Chemical yield of strontium was 90–95%.

The activity of <sup>90</sup>Sr was measured using a beta-radiometer RUB-01P consisting of a measuring device UI-38P1 with a detection unit BDZHB-06P1. The minimum measurable activity of <sup>90</sup>Sr during exposure of 1800 second was 0.7 Bq (for flat samples). The error strontium activity measurement was ± 25% at P = 0.95. Uranium, plutonium, and americium were detected by alpha-spectrometry after the ion exchange separation [3]. Uranium and plutonium were concentrated and separated on anion exchanger AB-17-8 in Cl-form obtained from 9 mol/dm<sup>3</sup> of HCl.

Americium and curium were purified by stepwise elution from cation exchange column (KU-2–8 in NH<sub>4</sub> – form) by α-hydroxyisobutyric acid with pH = 4.75. To determine the chemical yield of uranium, plutonium, and americium the tags <sup>232</sup>U, <sup>242</sup>Pu, and <sup>243</sup>Am were introduced. The alpha-spectrometric measurements were made using an eight-channel alpha spectrometer manufactured by *EG&G ORTEC OCTETE PC* with silicon semiconductor detectors of BU-017-450-100 ULTRA series having a detection efficiency of 25% at a distance of 12 mm from the source. The background for energies above 3 MeV did not exceed 1 impulse / hour. Mass concentration of uranium in water was set by the photometric

method in the form of uranyl complex with arsenazo III [4].

The content of organic (polymeric) substances in the original solution and in the filtrate was determined by bichromate oxidizability technique [5].

#### **DRAIN WATER PURIFICATION FROM ORGANIC COMPOUNDS, TRANSURANIC ELEMENTS, AND URANIUM**

The sizol group preparations (hereinafter referred to as «sizol») are highly effective aluminum and silicon bearing agents which provide the most integrated purification as compared with the other known coagulants due to more complete flocculation at a much higher speed of its course [6].

The coagulants are compounds capable of being hydrolyzed in water and forming various high-absorbing structures. Colliding with flakes of hydrolyzed coagulant the colloidal particles of dirt are adsorbed by them or mechanically captured by loose flake aggregates and precipitate together. In addition to the adhesion of colloidal particles, the molecular absorption of organic impurities, as well as the chemisorption may occur on the flake surface. Completeness and rate of water clarification depends on the properties of the coagulant and the contaminants.

The considered substances intensify the separation of suspensions into solid and liquid phases and improve the quality of filtration or sedimentation.

When sizol is introduced to water during purification, as a result of sizol dilution there are created the conditions for raising  $pH$  and forming colloidal aluminum hydroxide that possesses a huge active surface. The polluting particles are absorbed on the surface through precipitation. The silica sol particles act as condensation nuclei for aluminum hydroxide coagulating sols and promote faster growth of their particles. In other words, the silica sol is a sort of flocculant that significantly accelerates coagulation. Furthermore, the presence of silica sol in reagent causes the formation of aluminum hydroxide at lower  $pH$ .

We have studied the possibility of creating an effective process for the purification of the *Shelter*

facility radioactive waters from organic compounds and uranium simultaneously reducing the share of secondary waste. The objects of the study were the waters containing salts, surface-active agents (surfactants), film-forming and complexing agents, mineral oils, other organic compounds and products of their degradation. The uranium content has been measured for two samples: it is equal to 12 and 34  $dm^3$ ; their  $pH$  ranges within 9.63–9.18.

The influence of  $pH$  and amount of sizol added (6.5% solution by weight) on COD, uranium concentration in filtrate and on weight (share) of dry sludge is illustrated in Table 1 [7, 8]. On the addition of 20–30 ml of sizol having a  $pH$  of 7.6 at a temperature of 30 °C to 1  $dm^3$  of radioactive water from the *Shelter* facility with uranium content of 12  $dm^3$  the following indicators have been reported: COD decreases from 2500 to 270–320  $mg O_2/dm^3$ ; purification effectiveness makes up 87–89%; uranium concentration falls to 2.7–2.8  $dm^3$  at purification effectiveness of 76–77%; dry residue weight amounts to 0.359–0.371 g in the case of clarification on filter paper and on membrane (with a pore size of 0.2 micron), whereas the share of dry residue accounts for 0.0359–0.0371% of original water weight.

Similar data were obtained also for clarification of radioactive water from another premise of the *Shelter* facility. On the addition of 20–30 ml of sizol at a temperature of 10–20 °C to 1  $dm^3$  of radioactive water with uranium content of 34  $mg/dm^3$  the following data have been obtained: COD decreases from 2100 to 35–40  $mg O_2/dm^3$  for purification effectiveness of 98%; uranium concentration falls to 9.2–9.5  $dm^3$  at purification effectiveness of 72–73%; dry residue weight amounts to 0.300–0.305 g, whereas the share of dry residue accounts for 0.0300–0.0305% of original water weight.

These data obtained with the use of sizol have been compared with the other data received earlier for the *Shelter* facility [7, 8].

The same radioactive water samples were treated with lime milk having a  $pH$  of 10–11 and then

with solution of  $\text{FeCl}_3$  (600 mg) and with polyacrylamide solution (0.6 mg). As the treated sample settled for 1 day the weight content of organic matter in thickened suspension amounted to 1100–1400  $\text{mg O}_2/\text{dm}^3$  at a purification effectiveness of 43–52%. Uranium concentration in the clarified water decreases from 12–34 to 7.0–21  $\text{dm}^3$  at a purification effectiveness of 39–42%, and the share of dry residue extracted by filtration of clarified water through a filter paper makes up 0.52–0.58% of original water weight.

The new method for radioactive water purification proposed herein has considerable advantages as compared with the known technique. It gives a significantly greater effectiveness of purification from organic compounds, including the polymer products (siloxane-acrylate binder and other hard-to-remove substances: ionic surfactants, mineral oils, and other compounds) and uranium at a lower sizol consumption.

A significant advantage of using sizol is decreasing share of secondary waste (dry residue weight).

At the next stage of research, three samples of radioactive water from the *Shelter* premises were treated with coagulant flocculant sizol (6.5% solution) having a *pH* of 6–7. The optimum amount of sizol, 20–30 ml per 1  $\text{dm}^3$  of LRW, was added. Then, the filtrate sample was catalytically oxidized by hydrogen peroxide. The samples were heated to 70–80 °C, with iron sulfate (II) and hydrogen peroxide being added while stirring. The molar ratio of  $\text{H}_2\text{O}_2$  to organic substance accounted for 1:1, while that to  $\text{Fe}^{2+}$  was equal to 50:1. The oxidation time was 1 hour [9].

Tables 1–3 give the results of integrated treatment of original radioactive water samples. The comparison of data from these Tables shows that the use of method comprising the treatment with sizol, the catalytic oxidation by hydrogen peroxide, and the subsequent ultrafiltration leads to a significant decrease in the content of polymeric, other hard-to-remove organic substances, TRU, and uranium and substantially reduces the amount of secondary waste [9]. At the final stage, the pilot tests of developed method for purifying the

*Shelter* radioactive water have been conducted at the chemical plant of Chornobyl NPP.

The effectiveness of techniques for purification from organic (polymer) materials, including the dust-suppressive emulsion (siloxane-acrylate binder), as well as TUE and uranium has been determined [9].

The pilot plant has the LRW consumption ( $V = 300 \text{ dm}^3$ ), the precipitation ( $V = 300 \text{ dm}^3$ ), and the accumulation ( $V = 150 \text{ dm}^3$ ) containers. The plant is provided with metering and transfer pumps and with stop and control valves for dispensing the reagents. It has mixing devices as well as filters for pressure, ultrafiltration, and mechanical purification in different modes. The drain water from the drain-water tank of the 3<sup>rd</sup> reactor (sample BTV-3) and from the room 0005 (sample 0005) was used for the experiment.

This water contain different amount of radioactive water from the *Shelter* facility. The following reagents were used: hydrogen peroxide, iron sulfate (II), and nitric acid. For purifying the radioactive water the following appliances were used: a filter cartridge with a filtration surface of 0.08  $\text{m}^2$  equipped with a membrane filter with a 0.2 micron pore diameter; an ultrafiltration plant with filtering area of 0.08  $\text{m}^2$  equipped with a filter membrane PS-100 made of aromatic polyamide with a pore size of 0.08 microns.

During the test, while stirring, sizol (6.5% solution) was added to the drain water at the rate of 10  $\text{dm}^3$  per 1  $\text{m}^3$  of water. As the suspension settled, the clarified water was filtered through the

Table 1

Characteristics of Radioactive Water from the *Shelter* Facility

Sample	Chemical oxygen demand, $\text{mg O}_2/\text{dm}^3$		
	Original	Treated with sizol	After catalytic oxidation
1	2400	240	40
2	7000	510	30
3	5200	460	40

cartridge filter or by the ultrafiltration unit. At the same time, the drain water was purified using sizol (10 dm<sup>3</sup> per 1 m<sup>3</sup> of water) and by the catalytic oxidation by hydrogen peroxide at a *pH* of 4. The molar ratio of H<sub>2</sub>O<sub>2</sub> to organic substance was equal to 1 : 1, whereas that of H<sub>2</sub>O<sub>2</sub> to Fe<sup>2+</sup> made up 50 : 1. The oxidation lasted 1 hour.

Thereafter, the water was filtered through a membrane with a pore diameter of 0.2 microns.

The content of organic (polymer) substances in the original drain water and in the water after each stage of its treatment was determined on the basis of COD and activity of alpha emitters. The results are showed in Table 4 below.

The purification of drain water from organic substances, including from siloxane-acrylate binder and from other hard-to-remove substances using sizol with subsequent ultrafiltration has proved itself to be highly effective. COD of filtrate is 6–40 mg O<sub>2</sub>/dm<sup>3</sup> (purification effectiveness 95.8–99.4%). A significant advantage of the proposed method is effective removal of TRU: the activity of <sup>238+239+240</sup>Pu decreases by 95.7–99.8%; that of <sup>241</sup>Am falls by 90.5–99.8%; and that

of <sup>244</sup>Sm down by 94.6–95.7%. The effectiveness of purification from uranium is 92.1–98.1%.

However, the method has the following disadvantage. It has been established that the treatment of drain water with sizol leads to the formation of thickened suspension and clarified liquid. The purification of clarified liquid on a membrane having a pore size of 0.2 microns is highly effective. At the same time, the effectiveness of filtration of thickened suspension on the same membrane filter decreases 5–7 times. To increase the process effectiveness filter aids have been used [10].

The filter aids are finely dispersed liquid permeable materials intercepting the solid particles. For purification of hard-to-filter suspensions the filter aids are preliminarily applied to the septum, which prevents clogging of its pores by particles of suspension. Before the filtration, the filter aids are added to the original suspension thereby improving the structure of resulting precipitate and reducing its resistivity. Among the filter aids, there are diatomite, perlite, cellulose, wood flour, asbestos, and mixtures of some of these materials. When selecting filter aids empirically the re-

Table 2

Content of Radionuclides in Original Samples of Radioactive Drain Water from the Shelter Facility

Sample	Activity, Bq/dm <sup>3</sup>					Uranium concentration, mg/dm <sup>3</sup>
	<sup>137</sup> Cs	<sup>90</sup> Sr	<sup>238+239+240</sup> Pu	<sup>241</sup> Am	<sup>244</sup> Cm	
1	9.7 · 10 <sup>6</sup>	1.9 · 10 <sup>6</sup>	3.3 · 10 <sup>3</sup>	3.4 · 10 <sup>4</sup>	1.1 · 10 <sup>3</sup>	9.0
2	2.2 · 10 <sup>6</sup>	2.9 · 10 <sup>5</sup>	2.2 · 10 <sup>3</sup>	6.2 · 10 <sup>3</sup>	1.8 · 10 <sup>2</sup>	2.1
3	3.6 · 10 <sup>7</sup>	3.0 · 10 <sup>7</sup>	1.6 · 10 <sup>4</sup>	5.5 · 10 <sup>5</sup>	2.0 · 10 <sup>4</sup>	180

Table 3

Content of Radionuclides in Original Samples of Radioactive Drain Water from the Shelter Facility after Integrated Treatment

Sample	Activity, Bq/dm <sup>3</sup> (purification effectiveness, %)			Uranium concentration, mg/dm <sup>3</sup> (purification effectiveness, %)
	<sup>238+239+240</sup> Pu	<sup>241</sup> Am	<sup>244</sup> Cm	
1	1.3 · 10 <sup>2</sup> (96.1)	1.6 · 10 <sup>3</sup> (95.3)	5.9 · 10 <sup>1</sup> (94.6)	2.8 (68.9)
2	9.4 · 10 <sup>1</sup> (95.7)	3.2 · 10 <sup>2</sup> (94.8)	9.1 · 10 <sup>1</sup> (94.9)	0.13 (93.8)
3	3.7 · 10 <sup>1</sup> (99.8)	2.3 · 10 <sup>4</sup> (95.8)	8.6 · 10 <sup>2</sup> (95.7)	33 (81.7)

searchers are primarily guided by requirement for purity of ready filtrate.

In [11], it has been showed experimentally that the use of wood flour (grades 140 or 180 according to GOST 16391-87) can significantly increase the rate of filtration of thickened suspension and ensure a highly purified filtrate. Having been filtered the precipitate containing organic (polymeric) materials, including siloxane-acrylate binder and other hard-to-remove substances, insoluble salts, oxides of silicon and aluminum, wood flour, and radionuclides is dried at a temperature of 105 °C and burnt at a temperature over than 700 °C. This precipitate burns with formation of radioactive aerosols caught by Petryanov multilayer filters [12]. After the combustion of filtered precipitate the amount of ash per 1 dm<sup>3</sup> of drain water is 0.020–0.046 g, while its weight percentage is 0.002–0.0046% of water. The *Solka-Floc* cellulose manufactured by *Dicalite* can be used instead of wood powder.

The present study was conducted in 2010–2011. It shows that the pre-treatment method with the use of coagulant-flocculant, catalytic oxidation by hydrogen peroxide, and ultrafiltration makes it possible to avoid disruptions of the

process on evaporators in the course of drain water treatment. The proposed method prevents clogging of evaporators by siloxane-acrylate binder and other organic substances vulcanized by heating. The removal of alpha-emitting radionuclides enhances safety of LRW solidification.

**PURIFICATION OF DISTILLATION RESIDUE FROM ORGANIC COMPOUNDS, TRANSURANIC ELEMENTS, AND URANIUM**

The specific features of distillation residue oxidation treatment from organic compounds, TRU, and uranium using hydrogen peroxide, potassium permanganate, and ultrafiltration have been studied [14].

The LRW residue taken for the research has the following characteristics: organic matter: 7.4–15 g/dm<sup>3</sup>; COD: 6000–9500 mg O<sub>2</sub>/dm<sup>3</sup>; inorganic salts: 50–251 g/dm<sup>3</sup>; and pH = 13.1–13.5 [14].

Firstly, the distillation residue was oxidized by a 5% potassium permanganate solution with pH = 13.1–13.5, at a temperature of 70–80 °C during 3 hours. Then, the residue's pH was upped to 4 with the help of nitric acid. Thereafter, the residue was oxidized by a 5% solution of hydrogen peroxide in the presence of 1 g of FeSO<sub>4</sub> (as a cat-

Table 4

**Integrated Purification of Drain Water at Pilot Plant**

Sample	COD, mg O <sub>2</sub> /dm <sup>3</sup> (effectiveness of purification, %)	Activity, Bq/dm <sup>3</sup> (effectiveness of purification, %)		Uranium concentration, mg/dm <sup>3</sup> (effectiveness of purification, %)
		<sup>238+239+240</sup> Pu	<sup>241</sup> Am	
Original sample BTV-3	280	40	3.4 · 10 <sup>3</sup>	110
Purified BTV-3, 1 <sup>st</sup> method	80 (71.4)	1.7 (95.9)	76 (97.8)	52 (52.7)
Original sample 0005	960	530	6.3 · 10 <sup>3</sup>	610
Purified 0005, 1 <sup>st</sup> method	6–40 (95.8–99.4)	0.90–2.6 (99.5–99.8)	16–110 (98.3–99.7)	12–18 (97.0–98.0)
Purified 0005, 2 <sup>nd</sup> method	14 (98.5)	3.0 (99.4)	6.1 · 10 <sup>2</sup> (90.5)	48 (92.1)
Purified 0005, 3 <sup>rd</sup> method	18 (98.1)	2.3 (99.6)	13 (99.8)	11 (98.1)

Note. Purification techniques: no.1 treatment with sizol, filtration through a 0.2 micron membrane; no. 2 treatment with sizol, ultrafiltration through a 0.08 micron membrane; no. 3 treatment with sizol, catalytic purification by H<sub>2</sub>O<sub>2</sub>, and filtration through a 0.2 micron membrane.

alyst) per 1 dm<sup>3</sup> of residue at the same temperature. This process lasted 1 hour. The oxidation with potassium permanganate and hydrogen peroxide on the catalyst led to a decrease in COD from 6000–9500 mg O<sub>2</sub>/dm<sup>3</sup> to 1800–2300 mg O<sub>2</sub>/dm<sup>3</sup>.

Table 5 shows the results of oxidation of original distillation residue using the described method. The alternative catalytic purification by hydrogen peroxide (5 wt.%) and potassium permanganate (5 wt.%) with further ultrafiltration leads to a decrease in COD from 6000–9500 to 800–2000 mg O<sub>2</sub>/dm<sup>3</sup>, as well as reduces the activity of Pu isotopes by 74–87%, that of <sup>241</sup>Am by 94–95%, and that of <sup>244</sup>Cm by 90–95%; the effectiveness of purification from uranium reaches 94–99% [14].

When the distillation residue is oxidized, the complex organic compounds with metals decay. The radionuclides capable of participating in sorption processes transform into the ionic form [1].

Furthermore, iron hydroxides and manganese dioxide which are good absorbents for organic compounds and radionuclides are formed in the solution during purification.

Thus, the effectiveness of pre-treatment of LRW distillation residue from organic compounds, TRU, and uranium by permanganate and peroxide oxidation followed by ultrafiltration has been established. This is crucial for improving the technique of distillation residue treatment. The oxidation method was proposed for the implementation at the Chornobyl NPP, in 2009. At the final stage of research, the proposed method for oxidation treatment of residue was tested at a pilot plant [9]. The residue samples (A-201/3) were taken from tank A-201/3. The following reagents were used: potassium permanganate, hydrogen peroxide, ferric sulfate (II), and nitric acid. An ultrafiltration plant with a filtering surface of 0.08 m<sup>2</sup> equipped

Table 5

Characteristics of Distillation Residue

Subject of research	Activity, Bq/dm <sup>3</sup> (effectiveness of purification, %)					Uranium concentration, mg/dm <sup>3</sup>
	<sup>137</sup> Cs	<sup>90</sup> Sr	<sup>238+239+240</sup> Pu	<sup>241</sup> Am	<sup>244</sup> Cm	
Original distillation residue	1.9 · 10 <sup>7</sup>	3.2 · 10 <sup>6</sup>	1.6 · 10 <sup>3</sup>	9.6 · 10 <sup>3</sup>	4.7 · 10 <sup>2</sup>	17
Oxidized distillation residue	1.9 · 10 <sup>7</sup> (0 %)	3.0 · 10 <sup>6</sup> (6.3)	2.3 · 10 <sup>2</sup> (85.6)	6.4 · 10 <sup>2</sup> (93.3)	9.0 · 10 <sup>1</sup> (80.9)	2.4 (85.9)

Table 6

Integrated Purification of Distillation Residue at Pilot Plant

Distillation residue	COD, mg O <sub>2</sub> / dm <sup>3</sup> (effectiveness of purification, %)	Activity, Bq/dm <sup>3</sup> (effectiveness of purification, %)		Uranium concentration, mg/dm <sup>3</sup> (effectiveness of purification, %)
		<sup>238+239+240</sup> Pu	<sup>241</sup> Am	
Original distillation residue from A-201/3	2100	180	2,9 · 10 <sup>3</sup>	6100
Oxidized distillation residue, 1 <sup>st</sup> method	1600 (23,8)	170 (5,6)	2,3 · 10 <sup>3</sup> (20,7)	2600 (57,4)
Oxidized distillation residue, 2 <sup>nd</sup> method	390 (81,4)	36 (80,0)	18 (99,4)	1700 (72,1)

Note. Purification methods: no. 1 oxidation by potassium permanganate, ultrafiltration on a 0.08 micron membrane; no. 2 oxidation by potassium permanganate, ultrafiltration on a 0.08 micron membrane, catalytic oxidation by H<sub>2</sub>O<sub>2</sub>, filtration through a filter paper with a pore size of 3 microns.

with PS-100 membrane having average pore diameter of 0.08 microns was used to purify the radioactive water.

In the course of testing the method for purifying the distillation residue from organic (polymeric) substances and radionuclides, firstly, the residue was oxidized with potassium permanganate having a  $pH = 11.35$  at a temperature of  $85\text{ }^{\circ}\text{C}$  during 2 hours. As a result thereof, COD decreased from 2100 to 1600  $\text{mg O}_2/\text{dm}^3$ . The activity of  $^{241}\text{Am}$  in the clarified portion of residue fell by 20.7%; the effectiveness of purification from uranium accounted for 57.4%. The resulting oxidized product was filtered by the ultrafiltration unit. Then, the product underwent catalytic oxidation by hydrogen peroxide in acidic medium using concentrated nitric acid. This was accompanied with intensive formation of  $\text{CO}_2$  as a result of decomposition of metal carbonates and bicarbonates. Because of a threat of release of highly active residue into the premises of Chornobyl NPP chemical plant the catalytic oxidation by hydrogen peroxide was carried out under laboratory conditions: 300 ml of filtrate was taken after ultrafiltration and brought up to  $pH = 3.0$ . Then, 11 ml of hydrogen peroxide (34% solution) and 0.31 g of  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  were added.

The oxidation was carried out at a temperature of  $80\text{ }^{\circ}\text{C}$  during 1 hour. Having been treated with hydrogen peroxide the oxidized product was filtered through a *white ribbon* filter paper. After oxidation by permanganate and peroxide COD decreased from 2100 to 390  $\text{mg O}_2/\text{dm}^3$ , while the activity of isotopes significantly weakened:  $^{238} + ^{239} + ^{240}\text{Pu}$  by 80.0%,  $^{241}\text{Am}$  by 99.4%; the effectiveness of purification from uranium was 72.1% (Table 6).

### CONCLUSIONS

The research on purification of drain water and distillation residue from organic (polymeric) compounds and alpha-emitting radionuclides: plutonium, americium, curium, and uranium has been carried out. The experiments were performed with the use of radioactive water from the Chornobyl nuclear power plant. The project was im-

plemented stage by stage, including laboratory experiments and pilot tests.

A new method of drain water purification has been offered. It is based on the use of sizol-type coagulant-flocculant and the oxidation by hydrogen peroxide on ferric sulfate (II) catalyst with the subsequent ultrafiltration. This method prevents clogging of evaporators by siloxane-acrylate binder and other organic substances vulcanized by heating. As a result of decrease in content of alpha-emitting radionuclides, the safety of LRW solidification improves.

Another important component of research is experiments on purification of LRW distillation residue from organic (polymeric) compounds and alpha-emitting nuclides with further oxidation by potassium permanganate and hydrogen peroxide on ferric sulfate (II) catalyst and ultrafiltration.

Within the period from 29.10 till 02.11.2012, the IAEA expert mission visited Chornobyl to complete the technical specifications of the project on installation of water treatment plant for purification of the *Shelter* radioactive water and liquid radioactive waste from TRU and organic compounds to be financed by the European Commission within the framework of U4/01/11-C [15]. The technical specification provides for preliminary purification of the *Shelter* facility radioactive water from TUE and dust-suppressive emulsions (siloxane-acrylate binder) which are supplied to the special drainage system of the main building of the 3<sup>rd</sup> reactor and to the storage of liquid radioactive waste for subsequent solidification.

The project is based on the assumption that throughout the period of operation of the plant (at least, 30 years) the following tasks should be fulfilled:

- 1) All the necessary set of operations for acceptance, characterization, purification of the *Shelter* radioactive water from TUE and dust-suppressive emulsions, as well as the treatment of radioactive waste remaining after purification of water and distillation residue;
- 2) Acceptance and purification of the *Shelter* radioactive water from TUE and dust-suppressive



emulsions at the rate of, at least, 20 m<sup>3</sup> daily based on assumed accumulation of controlled and uncontrolled leaks at a rate of, at least, 5000 m<sup>3</sup> per year;

3) Acceptance and purification of distillation residue from TUE and dust-suppressive emulsions at a rate of, at least, 3.5 m<sup>3</sup> daily assuming that the capacity of LRW treatment plant is 2.5 m<sup>3</sup> daily;

4) The purification of the *Shelter* radioactive water and distillation residue should ensure the minimum possible amount of secondary radioactive waste not exceeding 5% of the volume purified.

The technical specification does not specify purification technique. The future contractor is recommended to familiarize itself with the report on pilot tests carried out at the Chornobyl NPP within the period from 2009 to 2012, including with the results of this research.

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ОЧИЩЕННЯ ТРАПНИХ ВОД І КУБОВИХ  
ЗАЛИШКІВ ВІД ОРГАНІЧНИХ СПОЛУК,  
ТРАНСУРАНОВИХ ЕЛЕМЕНТІВ ТА УРАНУ  
НА ЧОРНОБИЛЬСЬКІЙ АТОМНІЙ  
ЕЛЕКТРОСТАНЦІЇ

Стаття присвячена вивченню очищення трапних вод та кубових залишків від органічних (полімерних) сполук, трансуранових елементів і урану. Запропоновано спосіб попереднього очищення з використанням коагулянту-флокулянту типу «Сизол», каталітичного окислення пероксидом водню й ультрафільтрації. Зазначений спосіб запобігає закоксовуванню випарних апаратів пилепригнічуючими речовинами та іншими органічними сполуками, які вулканізуються при нагріванні. За рахунок видалення альфа-випромінюючих радіонуклідів підвищується рівень безпеки на атомній електростанції.

*Ключові слова:* трапні води, кубові залишки, Чорнобильська атомна електростанція, органічні сполуки, трансуранові елементи, уран.

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ОЧИСТКА ТРАПНЫХ ВОД И КУБОВЫХ  
ОСТАТКОВ ОТ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ,  
ТРАНСУРАНОВЫХ ЭЛЕМЕНТОВ И УРАНА  
НА ЧЕРНОБЫЛЬСКОЙ АТОМНОЙ  
ЭЛЕКТРОСТАНЦИИ

Статья посвящена изучению очистки трапных вод и кубовых остатков от органических (полимерных) соединений, трансурановых элементов и урана. Предложен способ предварительной очистки с использованием коагулянта флокулянта типа «Сизол», каталитического окисления пероксидом водорода и ультрафильтрации. Указанный способ предотвращает закоксовывание выпарных аппаратов пылеподавателем и другими органическими веществами, которые вулканизируются при нагревании. За счет удаления альфа-излучающих радионуклидов повышается уровень безопасности на атомной электростанции.

*Ключевые слова:* трапные воды, кубовые остатки, Чернобыльская атомная электростанция, органические соединения, трансурановые элементы, уран.

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