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ПОВЕДЕНИЕ УРАНА ПРИ ФОРМИРОВАНИИ И ПОСЛЕДУЮЩЕМ ХРАНЕНИИ ТВЕРДЫХ РАДИОАКТИВНЫХ ОТХОДОВ КОНВЕРСИОННОГО ПРОИЗВОДСТВА

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Проведен комплекс физико-химических исследований твердых радиоактивных отходов (РАО) приповерхностного хранилища конверсионного уранового производства. Установлено, что состав отходов представлен преимущественно соединениями кальция: гипсом, кальцитом и фторидом кальция. Уран содержится во всем объеме РАО. При этом по глубине залегания шлама он сконцентрирован неравномерно. Содержание урана в отходах составляет 0,005-0,65 масс.%. При формировании твердой фазы отходов уран преимущественно адсорбировался на поверхности основных компонентов шлама, часть его осаждалась в виде кальцийсодержащего уиксита $Ca_2(UO_2)_2(Si_2O_5)_3{\cdot}10H_2O$, уранофана-альфа $Ca(UO_2)_2(SiO_3OH)_2{\cdot}5H_2O$ и уранкалкарита $Ca(UO_2)_3CO_3(OH)_6{\cdot}3H_2O$. Изотопный состав урана, содержащегося в отходах хранилища, в пределах погрешности соответствует нормальному изотопному составу природного урана. Приповерхностное хранилище постоянно подвержено воздействию естественных природных факторов. Инфильтрация атмосферных осадков приводит к выщелачиванию из твердых РАО ряда компонентов, в том числе и урана. При этом он переходит в раствор в виде $[(UO_2)_2CO_3(OH)_3]^-$, $[UO_2(CO_3)_2]^{2-}$, $[UO_2(CO_3)_3]^{4-}$ и $Ca_2UO_2(CO_3)_3$. Последующая миграция урана с инфильтрующимися водами способствует его распространению в пределах всего шламового поля, включая рекультивационный слой грунта и приповерхностный водоем. В отдельных областях хранилища содержание урана в рекультивационном слое грунта достигает 0,043 масс.%. Концентрация урана в прудке составляет 17,97 мг/дм^3. Химический состав вод прудка характеризуется высоким содержанием хлорид-ионов (1,29 г/дм^3), кальция (630 мг/дм^3), сульфат-ионов (224 мг/дм^3), гидрокарбонатов (122 мг/дм^3). Водоем связан с грунтовыми водами, что повышает угрозу выхода загрязняющих веществ за пределы хранилища.

Ключевые слова: приповерхностное хранилище, радиоактивные отходы, уран, изотопный состав, физико-химические характеристики

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URANIUM BEHAVIOR DURING THE FORMATION AND SUBSEQUENT STORAGE OF SOLID RADIOACTIVE WASTES FROM CONVERSION PRODUCTION

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A complex of physicochemical studies of solid radioactive wastes (RW) of the near-surface storage facility from conversion uranium production was carried out. It has been established that the composition of the wastes is represented mainly by calcium compounds: gypsum, calcite, and calcium fluoride. Uranium is distributed throughout the entire volume of wastes. At the same time, uranium is unevenly concentrated along the depth of the sludge. The content of uranium in the wastes is 0.005-0.65 wt. %. Uranium was predominantly adsorbed on the surface of sludge by main components during the formation of the wastes solid phase. Uranium was partially precipitated in the form of calcium-containing weeksite $Ca_2(UO_2)_2(Si_2O_5)_3\cdot 10H_2O$***, uranophane-alpha*** $Ca(UO_2)_2(SiO_3OH)_2\cdot 5H_2O$***, and urankalcarite*** $Ca(UO_2)_3CO_3(OH)_6\cdot 3H_2O$***. The isotopic composition of uranium contained in the storage wastes corresponds, within the error, to the normal isotopic composition of natural uranium. Near-surface storage is constantly exposed to natural factors. Infiltration of atmospheric condensation leads to leaching of some components from solid RW. At the same time, uranium goes into solution in the form of*** $[(UO_2)_2CO_3(OH)_3]^-$, $[UO_2(CO_3)_2]^{2-}$, $[UO_2(CO_3)_3]^{4-}$ ***and*** $Ca_2UO_2(CO_3)_3$***. The subsequent migration of uranium with infiltrating water contributes to its distribution within the entire sludge field, including the reclamation soil layer and the near-surface pond. In some areas of the storage facility, the uranium content in the reclamation soil layer reaches 0.043 wt.%. The concentration of uranium in the pond was 17.97 mg*** L^{-1}***. The chemical composition of the pond water was characterized by a high content of chloride-ions (1.29 g*** L^{-1}***), calcium (630 mg*** L^{-1}***), sulfate-ions (224 mg*** L^{-1}***), hydrocarbonates (122 mg*** L^{-1}***). The pond is connected to groundwater, which increases the risk of pollutants escaping beyond the storage facility.***

Key words: near-surface storage facility, radioactive wastes, uranium, isotopic composition, physicochemical characteristics

INTRODUCTION

The Chepetsky Mechanical Plant SC - ChMP SC (Glazov, Udmurt Republic) is currently one of the largest in the world and the only Russian manufacturer of zirconium, hafnium, calcium products and low-temperature superconducting materials. The enterprise occupies a leading position in the production of niobium, titanium, and its alloys. However, the current environmental problems of the plant are associated with uranium manufacturing, which was organized at the enterprise in 1946 as part of the USSR Atomic Project and stopped in 2016 due to the decision to concentrate the entire sublimate cycle at the site of SChC SC (Seversk, Tomsk region).

Uranium production was removed, but the nuclear legacy remained. This legacy is a classic triad for nuclear industry enterprises, which were created in the 1940s - 1950s:

1) non-decommissioned buildings, technological sites and installations that were used for production of nuclear reactors fuel and other materials for defense purposes;

2) areas of radiation contamination remaining on the territories of technological sites;

3) significant volumes of radioactive wastes (RW) with high specific activity, accumulated in near-surface storages.

At the stage of organizing the uranium production, priority was given to the main goal – the creation of a nuclear bomb. Therefore, the solution of many environmental problems was relegated to the background. Currently, a lot of work is required to reduce the anthropogenic impact of the enterprise on the environment. And the most important task for ChMP SC is the conditioning of radioactive wastes located in the near-surface storage facilities of the plant.

The near-surface storage facility N 1 was built on the territory of ChMP SC in 1951 to dump solid radioactive wastes, and the near-surface facility N 2 was constructed in 1965. The latter is currently operational and is used to store wastes from other production of the enterprise. At the present time, the focus is on near-surface storage N 1, which was decommissioned in 1980. This storage received wastes from uranium, calcium, and zirconium productions. Therefore, the composition of wastes during the formation of its solid phase in the storage was heterogeneous. About 2 million tons of radioactive wastes have been accumulated in near-surface storage N 1 over the years of exploitation. This object is located on the left bank of the Cheptsa river near its bed. This river is a water artery for many settlements. Thus, the near-surface storage N 1 is a source of increased danger to the river ecosystem, as well as households and the health of the inhabitants of the Udmurt Republic. Currently, whole complexes of engineering solutions are used to prevent the ingress of harmful substances into the environment: the storage facility is surrounded by a system of fortifications, drainages, observation wells. However, an analysis of world experience has shown that such measures are often not enough. Near-surface storage facilities are exposed to natural factors, which leads to sludge weathering and leaching of various elements from RW [1-12]. The natural degradation of engineered barriers designed to contain radioactive particles can lead to their release beyond the perimeter of storage through infiltration into groundwater. The risk of these processes increases with the extension of the wastes storage period [10-15]. The consequences of radioactive isotopes release outside the storage are difficult to compensate, since the purification and regeneration of soils and water ponds from radionuclides requires the involvement of significant financial and labor resources [16]. Obviously, the damage to the health and well-being of citizens cannot be compensated at all. Therefore, the conditioning of radioactive wastes located in the near-surface storage facility N 1 of ChMP SC is an important environmental task today. In addition, the demand for nuclear power and for uranium increases every year. Rich deposits are gradually depleted, and there is a shortage of uranium, which is replenished only at the expense of stockpiles [17]. Therefore, radioactive wastes are a promising technogenic source of uranium for the needs of the nuclear industry.

It is first necessary to carry out a complex of physicochemical studies of RW accumulated in the near-surface storage N 1 of ChMP SC to specify the approaches to their conditioning and to assess the possibility of uranium extracting from sludge for further use in the nuclear fuel cycle. The purpose of this work is to determine the composition of radioactive wastes, to establish the forms of uranium in RW and the mechanisms of uranium precipitation during the formation of the solid phase, the zones of its concentration and migration activity during the wastes storage.

EXPERIMENTAL

Near-surface storage N 1 of ChMP SC consists of three sites separated from each other by dividing dams and protected by an external dike. Sampling was carried out from all three sites over the entire depth of the wastes (up to 7 m). The sludge samples were dried at 60 °C and dispersed in a ceramic mortar for further physicochemical studies.

The method of X-ray diffraction (XRD) analysis was used to establish the phase composition of solid radioactive wastes. XRD patterns of the samples were recorded using a STOE STADI P diffractometer (STOE, Germany). Qualitative analysis of XRD patterns was carried out using the ICDD PDF-2 Release 2016 X-ray powder diffraction database. Quantitative analysis was performed using the Rietveld method.

Chemical composition of radioactive wastes was determined by the method of wave X-ray fluorescence (XRF) analysis using an ARL ADVANT'X 4200W spectrometer (Thermo Scientific, Switzerland). The morphological characteristics of the surface of the RW samples were analyzed using scanning electron microscopy (SEM). The determination of the sludge composition was carried out using the electron probe microanalysis (EPMA). The samples were studied by SEM and EPMA using a two-beam electron-ion scanning microscope Auriga CrossBeam (Carl Zeiss, Germany) with an attachment for spectral X-ray microanalysis Oxford X-Max 80 (Oxford Instruments, UK).

A NexION 350X inductively coupled plasma mass spectrometer (Perkin Elmer, USA) was used for quantitative elemental analysis of the samples and to establish the chemical composition of waters from the near-surface storage. The content of fluoride, nitrate, and chloride-ions in solutions was determined by the potentiometric method using appropriate ion-selective electrodes. Concentrations of bicarbonate and carbonate-ions were determined by titration with 0.1 n solution of HCl in the presence of methyl-orange and phenolphthalein indicators. Determination of sulfate-ions was carried out by atomic emission spectrometry with inductively coupled plasma (ICP-AES) on an Optima 2100 DV (PerkinElmer, USA). The solutions were analyzed for sulfur content by ICP-AES method and then the obtained values were recalculated to sulfate-ion.

The VERTEX 70 (Bruker, Germany) instrument was used for infrared (IR) spectroscopic studies. IR-spectra were processed using Opus Version 6.5 software. Sludge samples were pressed into tablets with potassium bromide. The measurements of solid-phase specimens were carried out in the range of 400-4000 cm^{-1}.

The procedure for analyzing the isotopic composition of uranium included preliminary radiochemical preparation of samples (leaching of uranium from the sludge, sorption purification, electrodeposition on stainless-steel disk) and measurement using a Multirad-AS alpha spectrometer (STC “Amplitude”, Russia).

Leaching of uranium from solid radioactive wastes with distilled water was carried out in a laboratory reactor with stirring at temperature of 20-22 °C during 1 h. The weight of the sludge specimen for leaching was 50 g, and the volume of water was 0.25 L.

RESULTS AND DISCUSSION

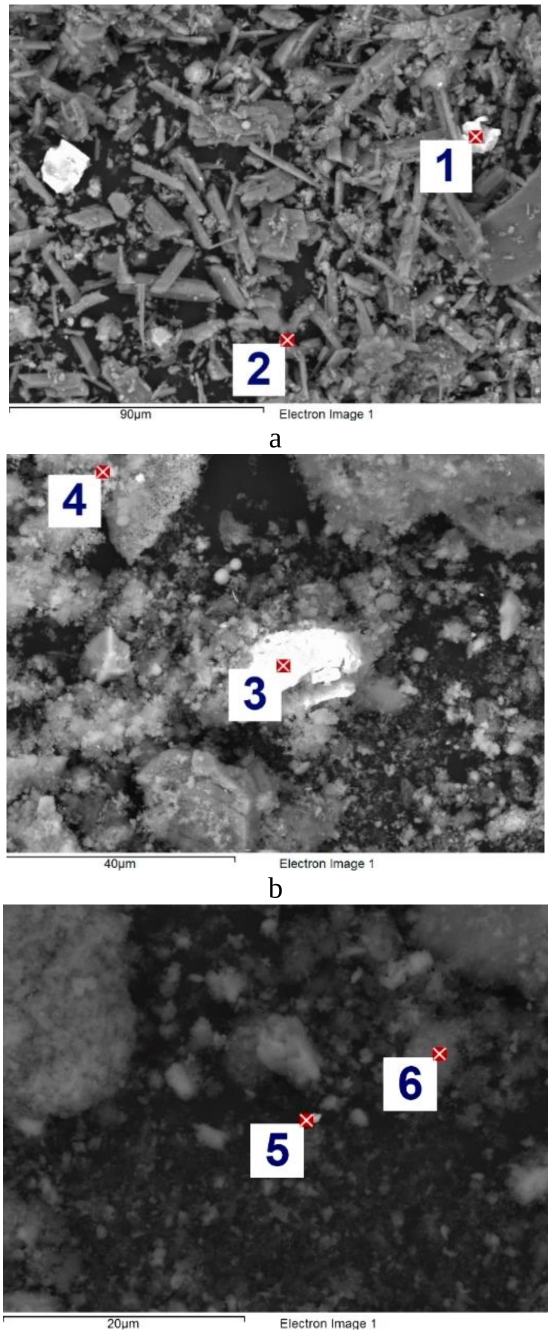
Near-surface storage N 1 of ChMP SC consists of 3 sites separated from each other by dividing dams. Site N 1 was used from 1951 to 1966 for the disposal of uranium production wastes, which was dumped into the center of the site, where a non-drying pond is currently located. Site N 2 was used from 1952 to 1980 for the discharge by hydrotransport of solutions and sludge from uranium, zirconium, and calcium production of ChMP SC. At the same time, zirconium and calcium manufacturing wastes were dumped separately. That is why site N 2 consists of two zones: zone 1 was used to dump of zirconium production wastes, and the zone 2 was used for calcium production wastes storage. Site 3 was operated from 1952 to 1975 to dump various hydrate sludges and dry wastes. The conservation of near-surface storage facility N 1 was carried out at the end of the exploitation life. The conservation procedure included dehydration of the accumulated wastes, followed by covering the territory with two layers of soil with a total thickness of 0.65 m. In the early 2000s, the thickness of the reclamation layer was increased by backfilling with soil mined using a dredger in the water area of the Cheptsa River to strengthen the isolation of radioactive wastes from environment.

According to research results, the thickness of the soil reclamation layer of the near-surface storage is 3-4 m. This layer mainly consists of quartz (more than 60 wt. %). The phase composition also includes alunogen, anorthite, albite, gismondine, muscovite, calcite, and gypsum. In addition, an increased content of Fe (2-6 wt. %) and Ti (0.3-0.6 wt. %) indicates the presence of titanium- and iron-bearing minerals in the reclamation layer. Also, uranium (0.001-0.045 wt. %) was identified in the composition of this soil layer.

Solid radioactive wastes are located below the reclamation layer of soil. The composition of RW is characterized by a high degree of heterogeneity both in terms of locations and depth of occurrence. On the territory of site 1, the predominant phase of the wastes located below the reclamation soil layer is $CaSO_4 \cdot 2H_2O$. Gypsum content in the sludge was 64-87 wt. % depending on the depth of occurrence. In addition, the RW contain 9-16 wt. % of calcite. The presence of calcite is due to the chemical composition of wastewater from uranium production and the method of their processing. Industrial effluents were characterized by a high content of sulfate-ions because of specific of the technological schemes used at ChMP SC for processing of uranium ores and concentrates. Wastewater was treated with lime milk containing up to 50% calcite before its discharging into the near-surface storage. Therefore, gypsum and calcium carbonate are the basis of the solid phase of uranium production wastes. According to results, the sludge also contains 2-13 wt. % of quartz. The content of uranium in the wastes of map 1 is 0.01-0.08 wt. %. At the same time, the high content of calcite and silicon in waste pulps led to the formation of calcium-containing weeksite $Ca_2(UO_2)_2(Si_2O_5)_3 \cdot 10H_2O$ in several zones of the sludge storage facility [18].

Uranium production wastes located in the near-surface storage are characterized by an increased content of Mn (1.39-3.82 wt. %) and F (0.98-6.36 wt. %). Several refining operations, including fluoride refining, were used at the ChMP SC to obtain nuclear-grade uranium. Fluoride refining wastes cause high fluorine content in the sludges. The appearance of Mn in sludge is explained using pyrolusite for uranium oxidation at the stage of leaching and indicates the presence of residues of the uranium ores leaching of in wastes. Mineral composition of ores supplied for processing also causes the appearance of Fe (1-4 wt. %), K (0.2-1.0 wt. %), As (0.1-0.3 wt. %), P (0, 1-0.2 wt. %), Pb (0.1-0.24 wt. %) in the waste sludge.

According to results of SEM and EPMA (Fig. 1a, Table 1), individual particles containing a large amount of Ba (10-50 wt. %) were found in the wastes from uranium production. There are As (0.7-1.1 wt. %), Pb (0.5 wt. %), U (0.14-0.26 wt. %) and Fe (0.9-19 wt. %) in the composition of these particles. Analysis of radioactive wastes samples using the energy dispersive spectrometry (EDS) method showed that As, Fe, Pb, U are distributed over the entire surface of the sludge. In barium-containing wastes, Ba is concentrated only in the form of individual particles of barium sulfate, which was used to separate radium during the processing of uranium ores.



a

b

c

Fig. 1. SEM images of particles and points of analysis by the EPMA method: a – uranium production wastes; b – zirconium production wastes; c - wastes of calcium production

Рис. 1. СЭМ-изображения частиц и точки анализа шлама методом РСМА: a – отходы уранового производства; b – отходы циркониевого производства; c – отходы кальциевого производства

Table 1

Results of analysis of sludge particles by SEM with EPMA (wt.%)

***Таблица 1.* Результаты анализа частиц шлама методом СЭМ с РСМА**

Element	Spectrum of the point					
	1	2	3	4	5	6
O	20	53	27	30	58	65
F	-	-	37	9.9	-	-
Mg	0.3	1.2	1.4	0.3	5.8	11
Al	0.7	2.7	0.6	-	0.8	1.5
Si	3.7	4.2	3.8	0.5	2.2	4.6
P	-	0.5	-	-	0.1	0.2
S	14	6.5	-	-	0.3	0.3
Cl	-	-	-	-	0.2	0.1
K	-	0.5	-	-	-	-
Ca	1.8	5.7	15	2.2	32	15
Ti	-	-	0.2	-	-	-
Zr	-	-	0.7	56	-	-
Mn	-	6.3	0.1	-	-	0.2
Fe	0.5	7.1	0.7	-	0.7	1.5
Ni	-	-	-	-	0.2	0.3
Cu	0.6	0.3	0.4	-	0.1	0.3
Nb	-	-	7.1	-	-	-
Mo	-	-	1.3	-	-	-
As	-	1.0	-	-	-	-
Ba	58	11	-	-	-	-
Pb	-	0.5	-	-	-	-
U	0.3	-	4.8	1.1	-	-

There is a layer of wastes from zirconium production at a depth of 4-5 m in zone 1 of site 2. The main phases of these wastes are calcite (about 60 wt. %) and calcium fluoride (more than 23 wt. %). As a results of chemical analysis, Zr was detected throughout the entire sampling depth of zone 1, while its maximum content (1.27 wt. %) was detected precisely in the sludge layer at a depth of 4-5 m. The presence of Mo (0.4 wt. %), Nb (0.1 wt. %) and Hf (0.01 wt. %) in this layer of sludge is associated with technological wastes generated during the zirconium production. According to SEM and EPMA (Fig. 1b, Table 1) there are separate large particles 10-20 μm in size, containing about 50 wt. % Zr and 0.1-1.0 wt. % U. In addition, a significant number of points were found on the surface of the sludge, where the zirconium content was 0.1-3.0 wt. %. It was established that Nb is concentrated on the surface of calcium fluoride, Mo, Zr, Cu, Mn, Fe, and a large amount of uranium (up to 4.8 wt. %) were found together with it. Points with a high content of Pb (6-29 wt. %), as well as points with a large percentage of Ba (9-36 wt. %), were found during analysis of individual sludge particles. In the detected particles, Ba is found together with U (0.3-0.6 wt. %) and Zr (1.2-3.0 wt. %). The source of U, Mn, and Pb in the sludge of zone 1 (site 2) is wastes from uranium production (residues after uranium leaching from ores). The content of uranium in this layer according to the results of chemical analysis is 0.44-0.65 wt. %. Uranium in the sludge is concentrated together with Zr, Mn, Pb in the form of individual particles, its content varies from 0.1 to 5.0 wt. %. Analysis of wastes samples by EDS method showed that Zr, Mo, Pb and significant amounts of uranium are distributed over the entire surface of the sludge.

Uranium production wastes are located below the layer of zirconium manufacturing wastes at a depth of 5-7 m. Gypsum (58-86 wt. %) is the predominant phase of these wastes. Sludge also contains calcite (5-12 wt. %) and quartz (6-23 wt. %). The content of uranium is 0.08-0.2 wt. %, and it is partially present in the form of $Ca_2(UO_2)_2(Si_2O_5)_3\cdot 10H_2O$ in several waste layers.

The layer of wastes from the calcium production of ChMP SC, consisting of calcite (more than 83 wt. %) and quartz (5-16 wt. %), and characterized by an increased content of Mg (8.71 wt. %), Cu (0.33 wt. %) and Ni (0.35 wt. %) is located at a depth of 3-4 m in zone 2 of site 2. Individual particles containing these elements (Fig. 1c, Table 1) were identified by SEM and EPMA. According to the EDS results, magnesium, nickel, copper, and uranium are distributed over the entire surface of the sludge. The content of uranium in this layer of wastes is 0.005-0.014 wt. %. At the same time, in a number of areas of this facility zone, uranium is partially present in the form of uranophane-alpha $Ca(UO_2)_2(SiO_3OH)_2\cdot 5H_2O$. This uranium mineral was part of the ore material processed at the enterprise. According to the technological scheme, cakes after uranium leaching from ores after washing were sent to a near-surface storage, and the identified uranophane-alpha may be part of the unleached uranium minerals. However, more probably, occurrence of this phase in the sludge is caused by formation of the compound from aqueous solutions supersaturated with calcite in the presence of silicon during the formation of a solid wastes phase [18]. Uranium production wastes are located at a depth of more than 4 m. They mainly consist of gypsum (80-88 wt. %). Calcite (3-7 wt. %) and quartz (2.7-7 wt. %) are also present in the sludge. The content of uranium in these wastes is 0.02-0.055 wt. %, the element partially present in the form of $Ca_2(UO_2)_2(Si_2O_5)_3\cdot 10H_2O$.

Sludges from zirconium and calcium productions were sent to a near-surface storage facility to prevent dust formation of uranium-containing wastes and reduce their specific activity.

Below the reclamation soil layer of site 3 (at a depth of more than 4 m) there are wastes consist mainly of calcite (62-76 wt. %) and are characterized by an increased content of Mg (6.6-10.2 wt. %), Ni (0.19-0.26 wt. %), Cu (0.23-0.88 wt. %) and Cl (more than 0.5 wt. %). This sludge also contains quartz (6-21 wt. %), gypsum (up to 1.5 wt. %), hilsherite and thaumasite (up to 27 wt. %). Uranophane-alpha $Ca(UO_2)_2(SiO_3OH)_2\cdot 5H_2O$ and urankalcarite $Ca(UO_2)_3CO_3(OH)_6\cdot 3H_2O$ were found in a number of wastes layers in this site of the sludge field. These minerals can be part of the uranium leaching cake, which was dumped into a near-surface storage facility. However, both uranophane-alpha and urancalcarite can precipitate from aqueous solutions supersaturated with calcite; therefore, considering the composition of radioactive wastes, the occurrence of these compounds during the formation of the solid phase of wastes is not excluded [18, 19]. As in the case of site 2, calcium production wastes were sent to this area of the storage facility to prevent dust formation of uranium sludge and reduce the radioactive background. The content of uranium in wastes is about 0.011 wt. %.

As a results of IR-spectroscopy, the main components of solid radioactive wastes were reliably identified. The IR-spectra of uranium production wastes (Fig. 2) contain characteristic for $CaSO_4\cdot 2H_2O$ adsorption bands, associated with vibrations of water molecules and sulfate-ion: 3547 and 3492 cm^{-1} (ν_{as}, H_2O), 3404 and 3242 cm^{-1} (ν_s, H_2O), 1686 and 1622 cm^{-1} (δ_s, H_2O), 1115 cm^{-1} (ν_{as}, SO_4^{2-}), 668 and 602 cm^{-1} (δ_{as}, SO_4^{2-}) [20, 21]. The presence of calcite in the composition of solid radioactive wastes causes the occurrence in the IR-spectra of bands belonging to the vibrations of the carbonate-ion: 2515 cm^{-1} ($2\delta_s + \delta_{as}$, CO_3^{2-}), 1798 cm^{-1} ($\nu_s + \delta_{as}$, CO_3^{2-}), 1434 cm^{-1} (ν_{as}, CO_3^{2-}), 874 cm^{-1} (δ_s, CO_3^{2-}), 712 cm^{-1} (δ_{as}, CO_3^{2-}) [21, 22]. The IR-spectra of the wastes also have absorption bands characteristic of silicon dioxide: 1023 cm^{-1} (ν_{as}, Si–O–Si), 798 and 779 cm^{-1} (ν_s, Si–O–Si), 520 and 468 cm^{-1} (δ, Si–O–Si) [23-25]. The absorption bands associated with vibrations of various bonds in uranium minerals are in the same wave intervals as the bands characteristic of calcite, quartz, and gypsum; therefore, they cannot be accurately determined by this method. At the same time, in the IR-spectra of wastes containing uranophane-alpha, there are bands characteristic of this mineral at 446 and 587 cm^{-1}, which are associated with deformation vibrations of Si-O-Si [26, 27].

As a results of XRD, uranium compounds were found only in a number of zones of the near-surface storage. However, according to chemical analysis and EPMA, uranium is contained in the entire volume of wastes located below the reclamation soil layer. At the same time, uranium is unevenly concentrated along the depth of the sludge, its content in the waste layers ranges from 0.005 to 0.65 wt. %. Uranium sedimented mainly because of co-precipitation with the main components of the sludge during the processing of the wastewater with lime milk without the formation of its own mineral phases. Uranium is able both to be adsorbed on the surface of calcite and gypsum and to be introduced into their structure at the stage of precipitation. In this case, the main process of the uranium transition to the solid phase is adsorption [28-32].

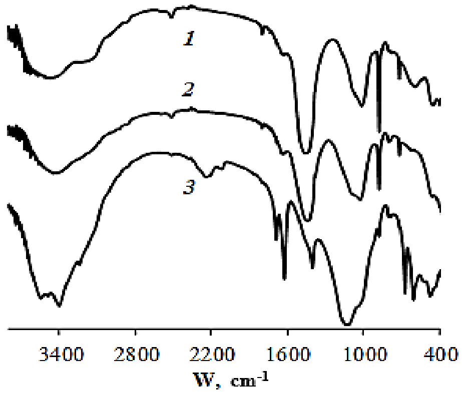


Fig. 2. IR-spectra of different types of wastes: 1 – wastes of calcium production (containing uranophane-alpha); 2 – wastes of zirconium production; 3 – wastes of uranium production

Рис. 2. ИК-спектры различных типов отходов: 1 – отходы кальциевого производства (содержащие уранофан-альфа); 2 – отходы циркониевого производства; 3 – отходы уранового производства

Near-surface storage is constantly exposed by natural factors. Infiltration of atmospheric condensation leads to leaching of uranium and other elements from solid radioactive wastes. The subsequent migration of uranium with infiltrating waters contributes to its distribution within the entire sludge field, including the reclamation soil layer. Uranium is adsorbed from soil water by components of the surface layer of the soil (quartz, zeolites, feldspars) and by compounds of solid radioactive wastes (calcite, gypsum, calcium fluoride). The degree of absorption is determined by the nature of the adsorbent and the form of uranium, which depends on the chemical composition and acidity of waters [31-38]. Results of investigation of uranium leaching with water from various wastes of storage facility showed that this element is actively extracted into solution even without the use of acidic or alkaline reagents. In this case, the concentration of uranium in the water phase rises with an increase in its content in the sludge (Table 2). Pregnant solutions obtained during uranium leaching from gypsum-containing wastes are characterized by a high content of sulfate-ions and calcium. In the case of wastes from zirconium and calcium production contained calcite as main phase, the concentration of bicarbonates in solutions is higher (Table 3). The pH value of the solutions after leaching is in the range 7-8 (Table 2). Uranium is present in pregnant solutions at such conditions in the form of $[(UO_2)_2CO_3(OH)_3]^-$, $[UO_2(CO_3)_2]^{2-}$, $[UO_2(CO_3)_3]^{4-}$ and $Ca_2UO_2(CO_3)_3$ [30, 33, 39]. The presence of the latter form enhances uranium migration because of limiting the U adsorption by any components of the reclamation layer of soil and radioactive wastes [39].

Table 2

Parameters of solutions obtained after uranium leaching with water from solid radioactive wastes

***Таблица 2.* Параметры растворов, полученных в ходе выщелачивания урана водой из твердых РАО**

Initial content of U in RW, wt. %	Parameters of solutions after leaching	
	Concentration of U, mg L^{-1}	pH
0.014	0.07	7.95
0.017	0.12	7.12
0.055	1.01	7.18
0.175	6.0	7.19
0.435	9.4	7.67

Table 3

Chemical composition of solutions obtained during the leaching of uranium with water from wastes of uranium (U), zirconium (Zr) and calcium (Ca) production, mg L^{-1}

***Таблица 3.* Химический состав растворов, полученных в ходе выщелачивания урана водой из отходов уранового (U), циркониевого (Zr) и кальциевого (Ca) производств, мг/дм^3**

Component	Type of wastes		
	U	Zr	Ca
Ca	503.3	44.5	29.9
Mg	76.8	48.5	60.2
Na	8.8	11.0	9.8
Al	0.72	0.73	0.71
Fe	10.7	6.2	5.8
Mn	0.15	0.11	0.11
Mo	9.1	17.1	0.10
U	6.0	9.4	0.07
HCO_3^-	122	229	366
SO_4^{2-}	3089	252	104
NO_3^-	7.7	26.2	1.3
Cl^-	17	28	22
F^-	4.7	11.1	3.1

The most active migration of uranium within volume of sludge due to infiltration of groundwater and atmospheric condensation was observed during near-surface storage exploitation period, when new portions of uranium wastes entered the sludge field every day. However, currently uranium is being redistributed between different layers of radioactive wastes and near-surface soil. Of particular concern is the migratory activity of uranium in the territory of site 1 of the near-surface storage. There is a pond in the center of site 1 fed by groundwater. This led to watering of wastes within the boundaries of this site and, as a result, to an increase in uranium migration. The concentration of uranium in soil water is 3-4 mg L^{-1}, in a pond water - 17.97 mg L^{-1}. The uranium content reaches 0.045 wt. % in the upper part of the reclamation soil layer of site 1. Chemical composition of soil water and pond water is characterized by a high content of calcium, sulfate-ions, and hydrocarbonates (Table 4). The pH value of soil water and pond water is 6.75 and 7.73, respectively. Thus, uranium is found in investigated waters mainly in the form of the above-mentioned carbonate complexes, it is adsorbed to a limited extent by the components of the soil and radioactive wastes and, as a result, accumulates in the pond.

An important criterion for evaluation the possibility to use of uranium contained in the RW of near-surface storage N 1 in the nuclear fuel cycle is its isotopic composition. According to the research results, the activity of uranium in RW is mainly caused by U-238 (0.045-0.064 Bq) and U-234 (0.043-0.066 Bq). In this case, the specific activities of these isotopes in the wastes samples are equal, within the error. Therefore, the isotopic composition of uranium contained in the solid RW of the near-surface storage N 1 corresponds to natural uranium [39].

Table 4

Chemical compounds of pond water and groundwater of site 1 of near-surface facility N 1, mg L^{-1}

***Таблица 4*. Химический состав вод прудка и почвенных вод шламового поля карты 1 хранилища, мг/дм^3**

Component	Pond water	Groundwater
Ca	629.8	646.7
Mg	34.9	92.0
Na	115.1	29.6
Al	0.66	2.1
Fe	7.87	13.4
Mn	1.03	31.8
Mo	0.94	1.7
U	17.97	3.36
HCO_3^-	122	381
SO_4^{2-}	224	388
NO_3^-	7.7	98.4
Cl^-	1287	29
F^-	2.6	3.1

CONCLUTIONS

Zones of location in the near-surface storage N 1 of ChMP SC of wastes from uranium, calcium and zirconium production were established in this work. The gypsum is predominant phase of the uranium manufacturing wastes. Calcite is identified as base phase of calcium production wastes. For zirconium production wastes main phases are calcite and calcium fluoride.

Solid radioactive wastes of storage contain 0.005-0.65 wt. % of uranium and it is distributed in the entire volume of wastes. At the same time, uranium is unevenly concentrated along the depth of the sludge. During the treatment of wastes effluents with lime milk, uranium passed into the solid phase mainly because of adsorption on the calcite and gypsum surface. In a few layers of solid radioactive wastes, uranium is present not only in connection with the components of the sludge, but also in the form of separate phases: calcium-containing weeksite, uranophane-alpha, and urancalcarite. These compounds were occured during the formation of the solid phase of the wastes during the treatment by lime milk.

The high migration activity of uranium determines its presence in the pond located in the center of site 1, as well as in the near-surface part of the reclamation soil layer, that increases the risk of radioactive substances leaving the storage facility. This is possible due to wind entrainment of solid particles from the surface of the sludge storage and water droplets from the surface of the pond, in case of extreme natural phenomena, as well as due to the migration of radionuclides into groundwater. Thus, the conditioning of radioactive waste placed in the near-surface storage facility N 1 of ChMP SC is an important environmental task today. The isotopic composition of uranium contained in the solid radioactive wastes of the storage corresponds, within the error, to the normal isotopic composition of natural uranium. Therefore, the wastes processing technology should include the associated extraction of uranium for its further use in the nuclear fuel cycle.

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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