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**SPECIATION AND MOBILITY OF URANIUM IN TAILINGS MATERIALS
AT THE U-PRODUCTION LEGACY SITE IN UKRAINE**

The results of the study on speciation and mobility of uranium in the ore processing residues in the Centralny Yar tailings (CY, former uranium processing site – Pridneprovsky Chemical Plant in Ukraine) are presented. Due to poor neutralization sludge material was dumped into the tailings body in acidic state. Several incidents with breakage in the pipeline transporting complex radiochemical solutions caused radioactive material spillover onto the tailings surface. Two features of radiological concern were identified – secondary contamination of the tailings surface amid elevated gamma dose rates, and excessive migration of radionuclides of U/Th decay series in strong acidic conditions within the tailings body. The monitoring data collected during 2005–2017 showed fast migration of uranium from the tailings body into the groundwater with specific activity varied in the range from 1 to 20 Bq/L. To support this finding the experimental studies aimed to obtain physical and chemical speciation of uranium in the tailings materials in existing and simulated conditions were undertaken. This was conducted by application of modified BCR sequential extraction methods followed by assessment of uranium speciation in equilibrium conditions, using the geochemical modeling tool MEDUSA coupled with the HYDRA database.

Keywords: Pridneprovsky Chemical Plant, uranium production legacy site, tailings residue, uranium speciation, sequential extraction method, groundwater contamination.

1. Introduction

The Centralny Yar (CY) tailings are one of the oldest tailings at the Pridneprovsky Chemical Plant (PChP), Kamyanske (Dneprodzerzhinsk in the past) in Ukraine, which were put into operation in the early 1950s. After filling the tailings facility with radioactive residues of uranium extraction, its surface was covered by local loam soils mixed with construction debris which were later planted with trees and bushes. Because the tailings materials were deposited into the natural ravine located at the upper Dnieper River terrace without the construction of any engineering protective bottom cover, seepage of the water contaminated by radionuclides from the tailings body into the local aquifer takes place.

The geological structure of the studied area comprise of crystalline basement overlaid by Quaternary deposits (alluvial sands, sandy loess). The thickness of sedimentary cover on the bottom of ravines is 12 - 15 m and up to 35 m at the watershed. In the geological section of this area, CY tailings belong to man-made deposits of uranium production residues (sand fractions), which are covered by local soils and construction debris (up to 2 m protective capping). These deposits fill the natural ravines with a maximum thickness of up to 15 m.

The hydrogeological conditions within the surrounding areas of the CY tailings are

characterized by the existence of two aquifers: Quaternary in alluvial sand and Precambrian in the fractured weathering zone of crystalline rocks. The body of the CY tailings is located in unsaturated conditions 12 m above the groundwater table of Quaternary aquifer and separated by the permeable loess thus making them hydraulically interconnected. The closest groundwater discharge points are situated at the Konoplyanka river about 900 m to the North of the tailings.

The upper cover of the CY tailings was installed aiming to physically protect the tailings material from atmospheric precipitations, to mitigate exhalation of ²²²Rn and dispersion of the contaminated materials from the tailings surface, but in fact, it cannot efficiently prevent water infiltration within the tailings body. Previous studies of Lavrova and Voitsekhovych [1] showed that poor quality and condition of the upper cover of the CY tailings cannot prevent excessive exhalation of ²²²Rn from the tailings body. The lack of the cover stability, percolated by the roots of deciduous trees planted here, provokes infiltration of atmospheric precipitation in the tailings body, which triggers acute downward migration of radionuclides.

The CY tailings facility has a surface area of about 2.4 ha and contains 0.22 million tons of uranium residues. The specific feature of the residue materials confined in CY is its strong acidic reaction

(pH 2.5 - 4.0) found throughout its body. Such conditions were formed due to two main factors: 1) filling with uranium extraction residue without applying a necessary chemical neutralization and 2) accidental spillage of pipelines [2].

The tailings residues conditions were preliminary studied by several Ukrainian institutions. First drilling campaign have been carried by the Ukrainian Scientific Research and Design Institute of Industrial Technologies in 2001 with the aim to estimate the amount of radioactive materials in the tailings bodies. Next drilling companies carried out during 2009 and 2012. The results of studies of this material reported in [1, 3, 4] allowed to preliminary estimate the vertical profiles of radionuclide distribution in the tailings bodies and consequently to present more accurate radionuclide inventory assessment for the tailings. Physical and chemical speciation of the radionuclides of U/Th series in the tailings materials from this site have also been studied by Protsak and Kashparov [5] and by Marynych et al. [6, 7].

The new data discussed in this paper are based on application of natural geochemical conditions laboratory procedures for sequential extraction of the uranium associated with the different physical and chemical complexes in the different compartment of the tailings body. This allowed to get better understanding of the parameters of uranium migration in the tailings body and its transfer to the groundwater with attempt to calculate the most favorable migration forms by the method of thermodynamical modeling.

2. Materials and methods

The samples of tailings materials were collected during several borehole drilling campaigns which were carried out in 2009 (boreholes: 1B, 2B, 3B, 4B, 5B, 6B, 09-1C, 09-2C) and in 2012 (12-1C and 12-2C) as a part of characterization studies undertaken under the remediation program for the PChP legacy site. The depth of the boreholes ranged from 12 to 18 m, drilled through the whole tailings body. The horizons for sampling were identified after a vertical gamma-rate survey carried out for each borehole. The moisture content of the material was measured in each 0.5m of the tailings materials columns. The representative samples taken from each of every 0.5 m of the core layers were sent to the laboratory to determine radionuclide content.

The tailings material from the CY is almost homogeneous with respect to the grain size distribution and represented by sandy-silt fractions with a mean particle size of about 0.03 mm. This is a loose material with a bulk density of 0.75 - 0.92 g/cm³ and

an effective porosity of 50 - 58 %. The density of the solid phase is practically uniform over the whole profile of the body of the tailings dump and equal to 2 g/cm³. Such parameters fully correspond to the material that remains after a technological cycle of the uranium processing. The hydraulic conductivity in the tailings body was estimated as about 3.3 cm/day. Mineralogical composition of tailings material was represented mainly by gypsum (~80 %) and quartz (~20 %).

At least three samples of each core were taken for analysis of the physical and chemical speciation of uranium in the tailings material. In order to identify the characteristic horizons in the tailings body for sampling and further analyses the data on moisture content in the tailings material, prior information about gamma dose rate vertical distribution were used. In total the materials from 10 boreholes at the different parts of the tailings body were studied. These samples were analyzed in two stages.

The first phase of the study was carried out by the Ukrainian Hydrometeorological Institute (UHMI) and Ukrainian Institute for Agriculture Radioecology (UIAR) in 2010, when the samples taken from 8 boreholes were studied using a 2-step extraction method which includes water-soluble (water as solvent) and exchangeable (1 mol L⁻¹ ammonium acetate) fractions [6].

The second phase of analysis was carried out in 2012 considering wider geochemical conditions which might take place at the CY tailings. The samples from selected horizons of two boreholes (12-1C and 12-2C) were used for a further analysis of a radionuclide speciation. For this purpose, the method of sequential extractions in accordance with BCR protocol (developed after EC Bureau of Certified Reference Material) was used [8]. Originally, this extraction method includes only three steps but the additional "water-soluble" step was added for comparing the results with the previous studies and scaling up this method to the natural processes in uranium tailings.

The four-step extraction method was used to evaluate a water-soluble, exchangeable and fixed (reducible and oxidizable) chemical speciation of radionuclides. The first step involves the extraction of water-soluble radionuclide compounds using deionized water. The second step includes a weak (0.11 M) acetic acid leaching of exchangeable forms. Next, the third and fourth steps of the extraction allow the study of fixed forms of radionuclides with Fe-Mn oxides and hydroxide complexes in the organic complexes of the tailings material respectively. For the third step of extraction, 0.1 M hydroxylamine hydrochloride was used as a leachate. The fourth step includes a

digestion with 8.8 M hydrogen peroxide and 1 M ammonium acetate extraction. The residuals after the last step showed the amount of radionuclides in the insoluble mineral compounds and was used to calculate the mass balance [9].

The data of hydrochemical and radionuclide composition in the groundwater (local aquifer and vadose zone) within the CY tailings was taken from technical reports of the long-term monitoring studies of UHMI.

The schematic layout of the spatial gamma dose rate distribution at the surface level of the tailings body as well as the locations of the boreholes used for sampling are shown in Fig. 1.

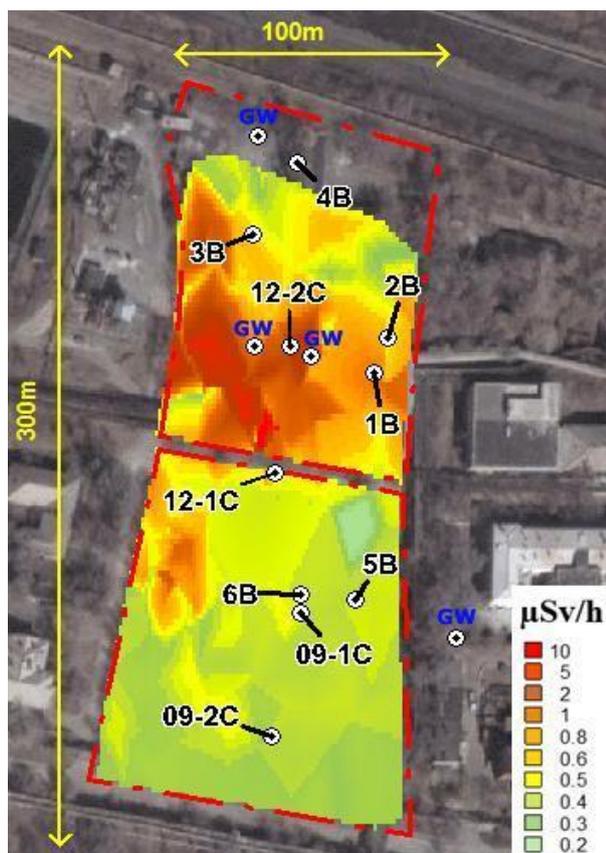


Fig. 1. Gamma dose rate on the surface of Centralny Yar tailings and location (with identity numbers) of boreholes used for sampling of the tailing materials ("GW" indicate the locations of the groundwater observation wells). (See color Figure on the journal website.)

The external gamma radiation dose rate on the surface of the tailing territory is varied in a wide range between 0.25 - 0.50 $\mu\text{Sv/h}$ at the relatively clean parts of its surface and from 1 to 10 $\mu\text{Sv/h}$ at the locations which were presumably affected by the accidental spillage of the contaminated uranium extraction residues transported via pipelines crossing the tailings.

The measurements of gamma-emitting radionuclides in solid samples and the extraction aliquots were carried out using a low-background HPGe

detector GMX40C, ORTEC. The methods of measurement are described by Bugai, et al., 2015 [3]. For validation of the results of the U-contents, representative samples were also determined using alpha-spectrometry methods following radiochemical separation procedures. All measurements were performed in the laboratory of Ukrainian Hydrometeorological Institute, which is certified by the International Atomic Energy Agency (IAEA) as a member of the IAEA ALMERA (Analytical Laboratories for the Measurement of Environmental Radioactivity) network [10].

For the purposes of calculating the equilibrium distribution of uranium species in the groundwater, the MEDUSA/HYDRA software suites were used [11]. An Eh-pH diagram of uranium speciation distribution was made based upon groundwater composition using the HYDRA hydro-chemical equilibrium constant database [11].

3. Results

3.1. Radionuclides vertical profiles

As noted above, the main feature of the geochemical state of materials in the tailings dump CY is the increased acidity of the U-ore processing residue (pH 2.5 - 4). This creates conditions for the leaching of uranium from the matrix of tailings materials and its washing out and selective vertical migration to the deeper horizons of the tailings body as well as contamination of the groundwater.

Recent studies allowed a specific activity concentration for radionuclides of U-Th decay series to be determined. In addition, ratios between activity concentrations of the radionuclides in the materials taken at the different parts and horizons of the tailings body were determined. These analyses allowed estimation of the spatial non-homogeneity of the radionuclide mobility speciations in the tailings body. The specific activities of the studied radionuclides in the tailings residues are shown in Table 1.

The vertical distribution of ^{238}U and ^{226}Ra activity in the tailings body column at different horizons is shown in Table 1. Radionuclide content in the cover materials of the tailings are close to background values, but slightly higher, probably due to the content of granitic debris.

The slightly increased content of ^{226}Ra and ^{210}Pb in the capping soils is a consequence of the residues from raw materials processing spilled on the surface during the accident at the slurry pipeline, which took place several times in the past.

The contaminated material on the surface of the tailings had no significant effect on the redistribution of uranium and radium content in the tailings body.

Table 1. Specific activities of selected radionuclides in different compartments of CY tailings (in Bq/g)

Layer (horizons)		Boreholes					
		12-1C			12-2C		
		Radionuclides					
		^{210}Pb	^{226}Ra	^{238}U	^{210}Pb	^{226}Ra	^{238}U
Cover		0.7	0.8	0.2	1.4	1.6	0.4
Tailings body	Upper layer	20	26	6	8	10	2
	Medium layer	83	113	5	73	83	21
	Bottom layer	75	83	16	3	5	10
Host geological environment		18	17	15	2	3	6

Higher gamma dose rates in the surface layer of an existing cover are evidenced by relatively high activity concentrations of ^{226}Ra (26 Bq/g) which was covered with a relatively clean local soils (content of ^{226}Ra - 0.8 Bq/g and less).

Distribution of radionuclides in the body of the tailings is more complicated. There are three main factors leading to the existing distribution: the initial composition of radionuclides in the residues of uranium production deposited in the tailings; geological, hydrogeological and geochemical conditions during a period of the tailings history (at the very beginning of production, during tailings facility fulfillment and after its closure); and

speciation and behavior of radionuclides in the different geochemical conditions.

The ^{226}Ra activity concentration in the upper layer of the tailings body exceeds uranium composition in the tailings materials by four times. It is assumed that acidic features of the spill materials stimulated mobility of the uranium from the sub-surface soil cover into the tailings body and its movement into the downward horizons of the tailings body.

The data shown in Fig. 2 may give a better understanding of U/Ra isotope disequilibria in the vertical profile and their distribution through the tailings body.

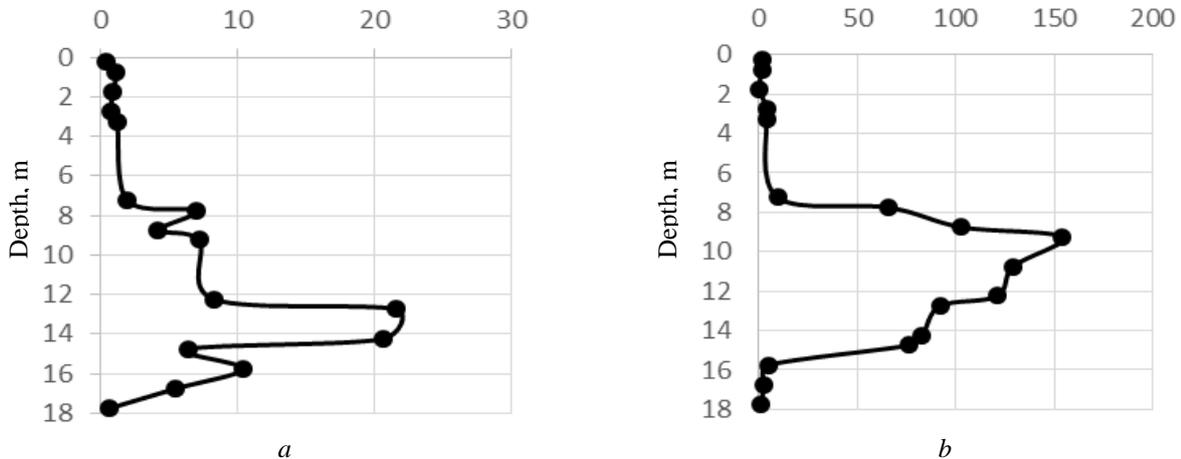


Fig. 2. Vertical profiles of the specific activity of ^{238}U (a) and ^{226}Ra (b) distribution in the borehole 12-2C of the tailings body.

Such vertical profiles of ^{238}U and ^{226}Ra are not only due to the fact that activity concentrations of radium are higher than uranium because later was simply extracted during ore processing, but also because their migration properties are different in the existing geochemical conditions in the tailings. It was found that the mobility ratio between uranium (^{238}U) and radium (^{226}Ra) in the-upper horizons of the tailings is 5, increasing to values in the range of 25 - 30 in the middle part and less than 1 at the bottom horizons of the tailings body. Furthermore, it was found that the front of uranium distribution is shifted down by ~2 m against radium and its

maxima corresponds to the most moist tailings horizons.

The main reason why ^{226}Ra has lower mobility in the tailings body is its precipitation with sulfate ions. As shown in a previous study of Marynych, et al. [6], there is a high concentration (3.7 - 5.6 g/L) of SO_4^{2-} in the pore water. With increasing content of SO_4^{2-} the total ^{226}Ra activity concentrations increases, but content of its mobile forms decreases.

This observation is in agreement with the results of physical and chemical speciation studies carried out in the tailings residue samples, which were collected from the different horizons of the tailings

body. According to this study the content of mobile forms decreases in the following order: $^{238}\text{U} > ^{210}\text{Pb} > ^{226}\text{Ra}$, meaning under geochemical conditions present in the CY tailings uranium shows the most mobile ability while radium is the least mobile.

3.2. Uranium speciation modelling

To study the physical and chemical forms of radionuclides in the tailings material a modified method of sequential extractions based upon BCR protocol was used [12]. The application of this method allowed estimation of the water-soluble, exchangeable and fixed forms of uranium in the tailings materials. The results of applying a modified sequential extraction method are shown in Fig. 3.

The results of uranium speciation studies in the tailings materials show the following. In most of the

samples, the uranium in the water-soluble fraction represents about 10 % while the uranium in exchangeable fraction reached up to 40%. Because a weak acetic acid was used for the second step of the extraction procedure, the exchangeable and water-soluble fraction could be combined into one group. This group was a readily exchangeable fraction, which could be washed out from the tailings body to the local aquifer by the infiltration of atmospheric water in the acidic environment of the tailings materials. The readily exchangeable group of uranium speciation includes oxides, carbonates, chlorides, and sulfates of uranium [13]. The largest amount of the uranium in the readily exchangeable forms was found in the lower horizons of the tailings body where the highest uranium activity concentrations in the vertical profile (see Fig. 2) were also observed.

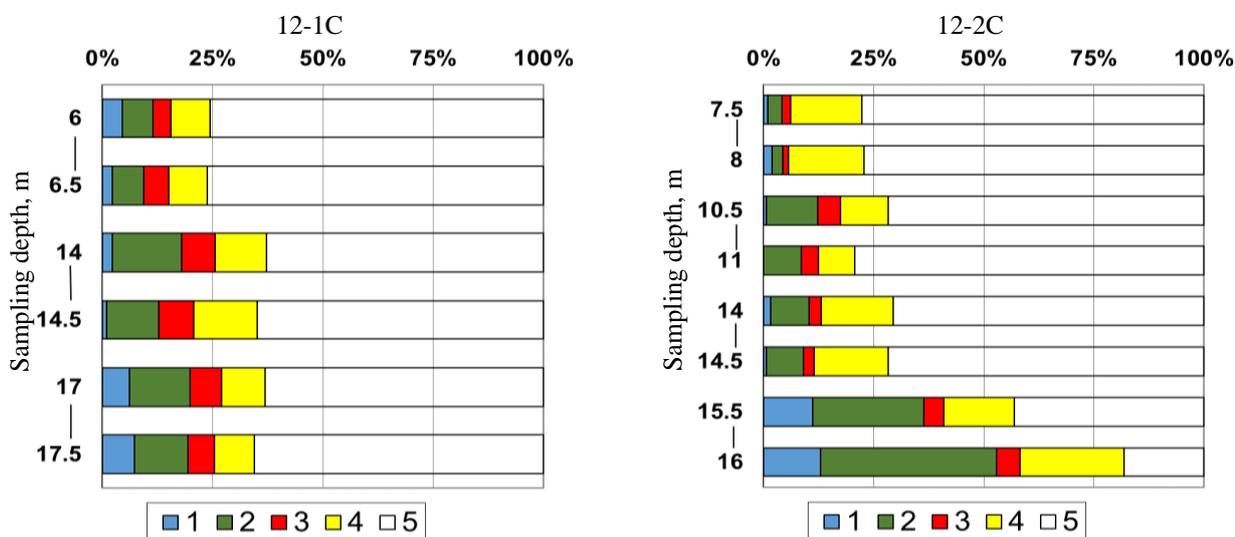


Fig. 3. Portions of ^{238}U activities associated with tailings material in the different mobile forms: 1 – water-soluble; 2 – exchangeable; 3 – in ferrum, manganum oxides and hydroxide complexes; 4 – in organic complexes; 5 – uranium in insoluble form. (See color Figure on the journal website.)

The next step of the sequential extraction method estimated the fixed fractions of uranium. The reducible fraction represents the uranium bound to ferrum, manganum oxides and hydroxide complexes and oxidizable fraction – uranium in organic complexes. The amount of reduced and oxidizable forms of uranium ranges from 1 - 8 % and 8 - 24 % respectively.

The possible factor determining the uranium retention with iron and manganese oxide and hydroxide complexes in the tailings body is a sorption of U(VI) in the pore water on oxides/hydroxides of iron [7, 14]. The lesser amount of readily exchangeable forms of uranium in the vertical profile of borehole 12-1C against 12-2C could be due to higher (average of 8 %) concentrations of ferrum, manganum oxides and hydroxide complexes in the pore water.

A higher portion of uranium content associated with organic complexes in oxidizable fraction (8 - 24 %) show that this fraction is insoluble in water and will be retained in tailings under natural conditions [15].

3.3. Spatial and geochemical modelling

Spatial modelling of pH distribution in CY tailings media was made on the results of measurements in water extractions from tailings material obtained from 2009 and 2012 drilling campaigns using the Kriging geostatistical method. The peculiar feature of the CY tailings as compared to the rest of the tailings sites on PChP is a strong acidic reaction of the media inside the tailing body. All the possible range of pH of the environment can be found at CY tailings site (pH 2.5 to 8), except strongly alkaline conditions with pH > 8 (Fig. 4).

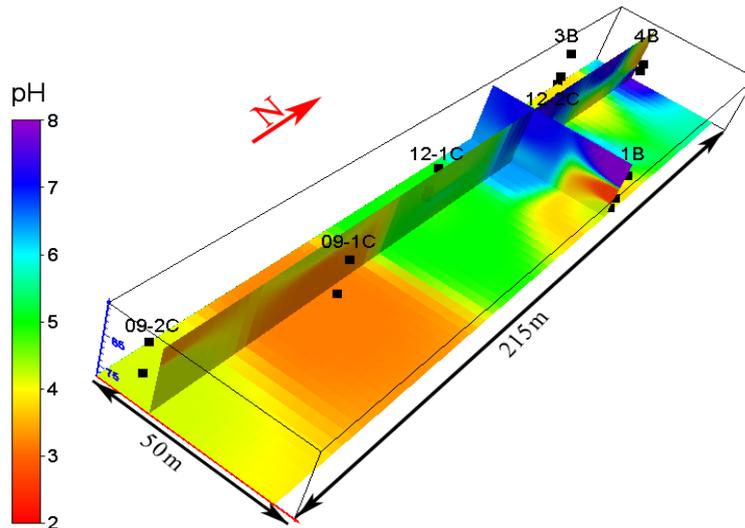


Fig. 4. Distribution of pH in CY tailings body. (See color Figure on the journal website.)

The results given in Fig. 4 demonstrate an existence of two specific areas in the tailings body, which are characterized by elevated acidic conditions with pH ranging from 3 to 5 and between 5 to 7. The low pH reactions in the tailings materials from the cell situated close to the production facilities (southern part) can be explained by poor neutralization of the residues, which took place at the initial production period, while the materials in the tailings cells situated at the northern part is less acidified. Presumably this is due to better neutralization of the tailings residues. The additional reason for the presence of some areas with high pH values (7 - 8) is soda neutralization of acid materials that were spilled to the tailings surface during accidents occurring on technological pipelines of uranium production facilities crossing the tailings.

The acid-base condition extrapolation model shown in Fig. 4 also displays that there has been a

reversal dependency between amounts of water-soluble forms of the uranium versus pH conditions. The maximum content of water-soluble forms corresponds to most acidic pH conditions that conform to the area with low pH range (pH 2.0 – 4.0) and elevated ^{238}U activity concentration in the water-soluble form given in Fig. 5. For low pH range pH 2.0 – 4.0 water-soluble fraction reaches 25 - 40 % of the total activity concentration of ^{238}U in tailings material, for pH 4.0 - 6.5 - 25 - 5 % and for pH 6.5 it is less than 5 %. Such distribution of pH conditions could be due different factors, but the main reason is that tailings were deposited gradually section-by-section from the south to the north with different levels of neutralization of residual production material. The upper layers of the central-northern part of the tailings is characterized by pH 6.5 – 8.0 where the amounts of water-soluble form of uranium is minimal probably due to its leaching downward into lower layers.

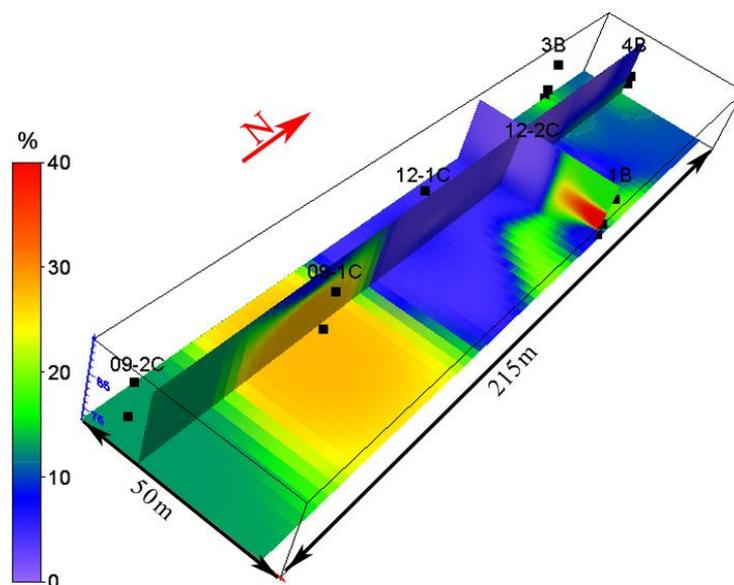


Fig. 5. Contribution of water-soluble fraction to the overall ^{238}U activity concentration in tailings material. (See color Figure on the journal website.)

The spatial distribution of the estimated pH values characterizing the tailings body corresponds well with the amount of the water-soluble fractions of uranium estimated in the tailings materials, which is presented schematically in Fig. 5.

Fig. 5 shows that the amount of the U-water exchangeable fractions in the materials taken from some sections of the tailings body increase from the surface horizons to the bottom layers of the tailings body.

It should be noted that the extrapolation results given in Figs. 4 and 5 were concluded with some uncertainties, taking into consideration the lack of input data for sufficient spatial analysis. Therefore,

Table 2. Mean hydrochemical composition of rainwater, pore water in the tailings material and groundwater in Quaternary aquifer under CY tailings

Environment	Total uranium in dissolved form, mg/L	Concentration, mg/L						
		Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻
Rainwater	ND	0.1	0.1	3.7	0.3	1	1.59	408
Porewater	7	239	23	618	550	61	2631	894
Groundwater	4	96	10	60	322	150	1493	500

Precipitation is the only surface water source within the territory of CY tailings, rainwater does not contain such high values of sulfate-ion compared to ground waters. It can be noted from Table 2 that tailings waters are the main source of groundwater contamination with sulfates and uranium as well. For the purposes of identifying the main occurring speciation, the geochemical modeling tool MEDUSA with HYDRA equilibrium database was used. The input data contains chemical parameters (pH and Eh), hydrochemical composition of water, and uranium concentrations. Geochemical modelling was conducted on averaged radiochemical and hydrochemical composition of porewater.

To determine the dominant speciation in the aqueous solution (pore water) the physico-chemical parameters of the water extractions from the tailings material were used. Table 3 shows the hydrochemical parameters and uranium composition in the water extraction form from different compartments of the CY tailings. The uranium value in Table 3 is percentage of the activity in the water extraction from the overall activity of the sample.

The positive range of Eh values listed in Table 3 is due to the presence of air during the extraction experiment, creating conditions in which the water is easily oxidized. These Eh values are almost similar to the values observed in natural conditions in the tailings. During the drilling campaign in 2012, the Eh parameter was measured directly in pore water supernatant from the core material [5]. As shown in Table 4, the values of Eh of pore waters tested in the field and water extractions measured in the lab are mostly similar, with no more than 0.1 V variation between values. It is anticipated that this variation

geochemical model simulation method was applied for further assessment, allowing determination of a ratio between the speciation of uranium in the tailings body and its migration capabilities to be removed in the vadose zone affecting groundwater contamination.

The main constituent anions in the hydrochemical composition of porewater and ground water within the CY tailings are sulfate-ion (up to 2.6 g/L of SO₄²⁻) and hydro-carbonate ion (up to 0.9 g/L of HCO₃⁻) The mean composition of rainwater, pore water and Quaternary aquifer is listed in Table 2.

will not make a big difference in terms of aqueous species of uranium, which can be assumed from the results of the modelling shown in Fig. 6.

Table 3. The portion of ²³⁸U in water soluble fraction from its total amount in the tailings materials in different geochemical conditions

Borehole	Sampling depth, m	pH	Eh, V	Uranium in water soluble fraction, %
09-2C	7.5 - 8	3.33	0.65	13.1
	17 - 17.5	4.17	0.61	12.9
09-1C	3.5 - 4	4.25	0.58	7.72
	15 - 15.5	3.17	0.71	27.6
3B	1.5 - 2	7.62	0.47	0.33
	11 - 12	3.79	0.57	8.15
	14 - 15	3.85	0.58	15.8
1B	2 - 3	7.87	0.45	16.8
	11 - 12	2.58	0.75	40.5
	15 - 16	4.18	0.60	6.91
4B	8 - 9	7.55	0.48	13.7
	5 - 6	3.44	0.52	5.77
12-1C	6 - 6.5	4.35	0.56	4.49
		4.81	0.65	2.20
	14 - 14.5	4.83	0.57	2.21
		5.92	0.59	0.93
	17 - 17.5	4.82	0.61	6.13
		4.85	0.65	7.34
12-2C	7.5 - 8	7.35	0.49	0.92
		7.42	0.50	1.99
	10.5 - 11	6.47	0.58	0.70
		14 - 14.5	4.73	0.61
	5.53		0.63	0.66
	15.5 - 16	7.50	0.50	11.1
		7.00	0.54	13.0

Table 4. Comparison between Eh values of the water extractions and porewaters tested in field

Borehole	Sampling depth, m	Water extraction	Porewater
		Eh, V	
12-1C	6 - 6.5	0.56	0.56
	14 - 14.5	0.57	0.47
	17 - 17.5	0.61	0.52
12-2C	7.5 - 8	0.49	0.45
	10.5 - 11	0.58	0.57
	14 - 14.5	0.61	0.52
	15.5 - 16	0.5	0.4

The results of the modeling shown in Fig. 6 show that at low pH conditions the uranium predominantly migrates in the form of sulfate UO_2SO_4 and uranyl carbonate compounds UO_2CO_3 , $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ that occur in a neutral and slightly alkaline pH range. The oxidation-reduction potential (Eh) is one of the key limitation factors of the uranium mobility. In general, we can find 3 main stability fields of the uranium equilibrium phases in

current conditions: the first one in all pH range below the 0.3 V of oxidation-reduction potential – field of crystalline precipitate of U_4O_9 and UO_2 , the second one in 1 - 5 pH range and above 0.3 V Eh – uranyl sulfate UO_2SO_4 , and the third one is from 5 to 9 pH and above 0.3V Eh – group of fractions in the form of carbonate complexes. Most of the tested samples showed that the main speciation in the aqueous solution of the CY tailings is uranyl sulfate UO_2SO_4 . Uranyl sulfate is equilibrium phase for acidic conditions, it is a very mobile water-soluble compound, and could be easily washed out from the tailings material with the infiltration of waters under oxidizable conditions. Infiltration of Rainwater through the CY tailings body might cause dissolution of uranium sulfate complexes and formation of uranyl carbonate compounds in the presence of HCO_3^- ions taking into account that pH for Rainwater in this region is typically 7.5. In such circumstances one could expect to have an extensive migration of above compounds into groundwaters of local aquifers.

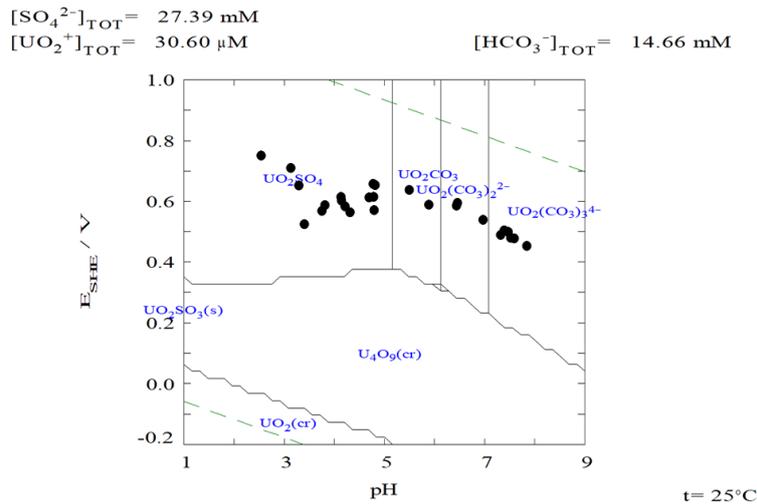


Fig. 6. Eh-pH diagram for the dominant uranium aqueous species of the dissolved uranium in the presence of SO_4^{2-} and HCO_3^- in pore water.

According to the monitoring data collected during 2005 - 2017, the uranium activity concentration in the groundwater in the different locations at the tailings body and in different seasons varied in the range from 1 to 5 Bq/L up to 20 Bq/L. This indicates the existence of active processes of the uranium leaching from the tailings body and its capability of migrating into the vadose zone and the groundwater [4]. Other major radionuclides of uranium decay series (^{226}Ra , ^{210}Pb , ^{210}Po) were measured in significantly lower concentrations below 1 Bq/L that corresponds to their low mobility in the tailings body experimentally proven by this study using the sequential extraction method.

4. Conclusions

1. This study showed that the amount of mobile forms of the studied radionuclides decreases in the order $^{238}\text{U} > ^{210}\text{Pb} > ^{226}\text{Ra}$. This means that under geochemical conditions (pH, redox conditions, hydrochemical composition) of the CY tailings uranium is the most mobile with capability to migrate in the groundwater. The amount of uranium losses from the tailings body is strictly dependent upon geochemical conditions. The key governing factors are pH and redox potential (acidic oxidizable conditions). These factors are less sensitive for radium mobility: the main retardation factor for radium migration is a high concentration of the

sulfate-ion in the pore water from the tailings material.

2. The results of uranium speciation studies using a sequential extraction method in the tailings materials shows the following. In most of studied samples the uranium in the water-soluble forms was found in the range of about 10 % while the uranium amount extracted with an exchangeable fraction reached up to 40 %. Exchangeable and water-soluble fraction could be combined into one group – readily exchangeable fraction that includes oxides, carbonates, chlorides, and sulfates of uranium. The amount of uranium bound to ferrum, manganese oxides and hydroxide complexes and uranium in organic complexes varied in the range of 1 - 8 % and 8 - 24 % respectively. In addition, this method elucidated a possible factor determining the uranium retention in the tailings body, a sorption of uranium in the pore water on oxides/hydroxides of iron, and the amounts of fixed forms which are potentially a source for further remobilization of uranium compounds.

3. Spatial geochemical modeling results showed that there was a reversible dependency between amounts of water-soluble forms of the uranium versus pH. The maximum content of water-soluble forms of uranium corresponds to the most acidic pH conditions in the tailings body. For low pH range from pH 2.0 - 4.0, ^{238}U activity in water-soluble fraction reaches 25 - 40 % from overall activity concentration of ^{238}U in tailings material, for pH 4.0 - 6.5 it is 25 - 5 % and for pH 6.5 it is

minimal. The strong acidic reaction of the materials within the tailings body promotes a uranium migration outside the core into the groundwater.

4. According to the thermo-dynamical modeling carried out in this study, uranium migrates in the tailings mainly in the form of sulfate UO_2SO_4 and uranyl carbonate compounds UO_2CO_3 , $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ - the most favorable mobile forms in current hydrochemical conditions.

Therefore, results of the study revealed vulnerability of the groundwater medium and a new protective cover should be established at the surface of the tailings body to prevent the release of radionuclides into the groundwater.

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ФОРМИ ЗНАХОДЖЕННЯ ТА ХАРАКТЕР МІГРАЦІЇ УРАНУ В МАТЕРІАЛАХ ХВОСТОСХОВИЩ ОБ'ЄКТІВ СПАДЩИНИ УРАНОВОГО ВИРОБНИЦТВА УКРАЇНИ

Представлено результати досліджень із визначення форм знаходження та характеру міграції урану в залишках уранового виробництва, накопичених у хвостосховищі «Центральний Яр» (колишнє уранопереробне підприємство «Придніпровський хімічний завод» в Україні). Унаслідок недостатньої нейтралізації залишковий матеріал виробництва було завантажено в тіло хвостосховища в кислому стані. Також були аварії пульпопроводу, що призводили до розливу радіоактивних матеріалів на поверхню хвостосховища. Унаслідок цього було встановлено дві радіологічні проблеми: вторинне забруднення поверхні хвостосховища, представлене підвищеним рівнем потужності експозиційної дози, та міграція радіонуклідів U/Th рядів у сприятливих для цього кислих окислювальних умовах. Дані моніторингу, зібрані протягом 2005 - 2017 рр., показали підвищену міграцію урану від хвостосховища у ґрунтові води з активністю в межах від 1 до 20 Бк/л. Для підтвердження даних спостережень було проведено експериментальні дослідження з метою визначення фізичних та хімічних форм знаходження урану в матеріалах хвостосховища на базі існуючих та модельних даних. Для цього було використано модифікований метод послідовних екстракцій BCR із подальшим визначенням рівноважних форм знаходження урану, використовуючи інструмент геохімічного моделювання MEDUSA з підтримкою бази даних HYDRA.

Ключові слова: Придніпровський хімічний завод, об'єкти спадщини уранового виробництва, хвостовий матеріал, форми знаходження урану, метод послідовних екстракцій, забруднення підземних вод.

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ФОРМЫ НАХОЖДЕНИЯ И ХАРАКТЕР МИГРАЦИИ УРАНА В МАТЕРИАЛАХ ХВОСТОХРАНИЛИЩ ОБЪЕКТОВ НАСЛЕДИЯ УРАНОВОГО ПРОИЗВОДСТВА УКРАИНЫ

Представлены результаты исследований по определению форм нахождения и характера миграции урана в остатках уранового производства, накопленных в хвостохранилище «Центральный Яр» (бывшее ураноперерабатывающее предприятие «Приднепровский химический завод» в Украине). Вследствие недостаточной нейтрализации остаточный материал производства погружался в тело хвостохранилища в кислом состоянии. Также были аварии пульпопровода, которые приводили к разливу радиоактивных материалов на поверхность хвостохранилища. В результате было установлено две радиологические проблемы: вторичное загрязнение поверхности хвостохранилища, представленное повышенным уровнем мощности экспозиционной дозы, и миграция радионуклидов U/Th рядов в благоприятных для этого кислых окислительных условиях. Данные мониторинга, собранные в течение 2005 - 2017 гг., показали повышенную миграцию урана от хвостохранилища в грунтовые воды с активностью в пределах от 1 до 20 Бк/л. Для подтверждения данных наблюдений были проведены экспериментальные исследования с целью определения физических и химических форм нахождения урана в материалах хвостохранилища на базе существующих и модельных данных. Для этого был использован модифицированный метод последовательных экстракций BCR с последующим определением равновесных форм нахождения урана, используя инструмент геохимического моделирования MEDUSA с поддержкой базы данных HYDRA.

Ключевые слова: Приднепровский химический завод, объекты наследия уранового производства, хвостовой материал, формы нахождения урана, метод последовательных экстракций, загрязнение подземных вод.

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