UDC 541.49:546.791.6+546.73 DOI: https://doi.org/10.15407/geotm2021.157.212

URANIUM SORPTION FROM RADIOACTIVE WASTE OF URANIUM ORE PROCESSING AT PRIDNEPROVSK CHEMICAL PLANT

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СОРБЦІЯ УРАНУ З РАДІОАКТИВНИХ ВІДХОДІВ ПЕРЕРОБКИ УРАНОВИХ РУД НА ПРИДНІПРОВСЬКОМУ ХІМІЧНОМУ ЗАВОДІ

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СОРБЦИЯ УРАНА ИЗ РАДИОАКТИВНЫХ ОТХОДОВ ПЕРЕРАБОТКИ УРАНОВЫХ РУД НА ПРИДНЕПРОВСКОМ ХИМИЧЕСКОМ ЗАВОДЕ

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Abstract. The research results were generalized regarding the possibility of uranium sorption from radioactive waste accumulated at Production Association “Pridneprovsky Chemical Plant” (PA PCP). The conceptual possibility was illustrated for sorption leaching of uranium from pulps produced by acidic leaching of radioactive waste dumped at Zapadnoye (Western) tailing impoundment using AMP anionite contained benzyl pyridinium functional groups (manufactured by Smoly State Enterprise). Uranium recovery was 70 % to 80 % during waste acidic leaching with the mixture of 15 % sulphuric and 1.5 % nitric acids. Application of sorption leaching allowed the recovery increase up to 15 %. Uranium recovery was assessed from upper ground and underground water of Centralny Yar tailing site using AM-p-2 strong base macroporous anionite (produced by Smoly SP) based on styrene-divinyl benzene copolymer with 2-hydroxyethyl-dimethylammonium functional groups. This tailing impoundment features acidic reaction of radioactive water since the pulp was almost not neutralized after ore processing. It poses an environmental hazard due to active uranium leaching from the tailing impoundment body and its ability to migrate into groundwater. It was found that the distribution factor may attain ~2 000 for uranium concentration 7 mg/l in interstitial water and 4 mg/l in underground water. Assessment results were given regarding uranium recovery from radioactively contaminated water accumulated in the basement of building No. 103 using phosphate cationite based on modified plant material. The building is extremely contaminated and of top-priority for treatment and further dismantling. Sorbent capacity by uranium achieved in static mode was ~20 mg/g with distribution factor ~4 800. The results obtained may be proposed as the reasoning for the method and technology intended to decontaminate polluted water before it would be pumped from underground rooms of building No. 103. The research performed has shown that application of sorption materials is the most expedient and promising method for selective uranium recovery when solving the problems of tailing site remediation and handling radioactive waste of the former Pridneprovsky Chemical Plant.

Keywords: Pridneprovsky Chemical Plant, uranium ore processing tailing sites, sorption, cationite, anionite

Production Union Pridneprovsky Chemical Plant (PU PChP) was among the first industrial facilities in the former Soviet Union engaged in processing various uranium ores and concentrates. For many years, it was the basic factory where new hydrometallurgical technologies were implemented for selective uranium recovery. During the factory operating period (1948-1991), nine radioactive tailing impoundments were

formed; Figure 1 illustrates their location in the city of Kamianske and the region [1-3].

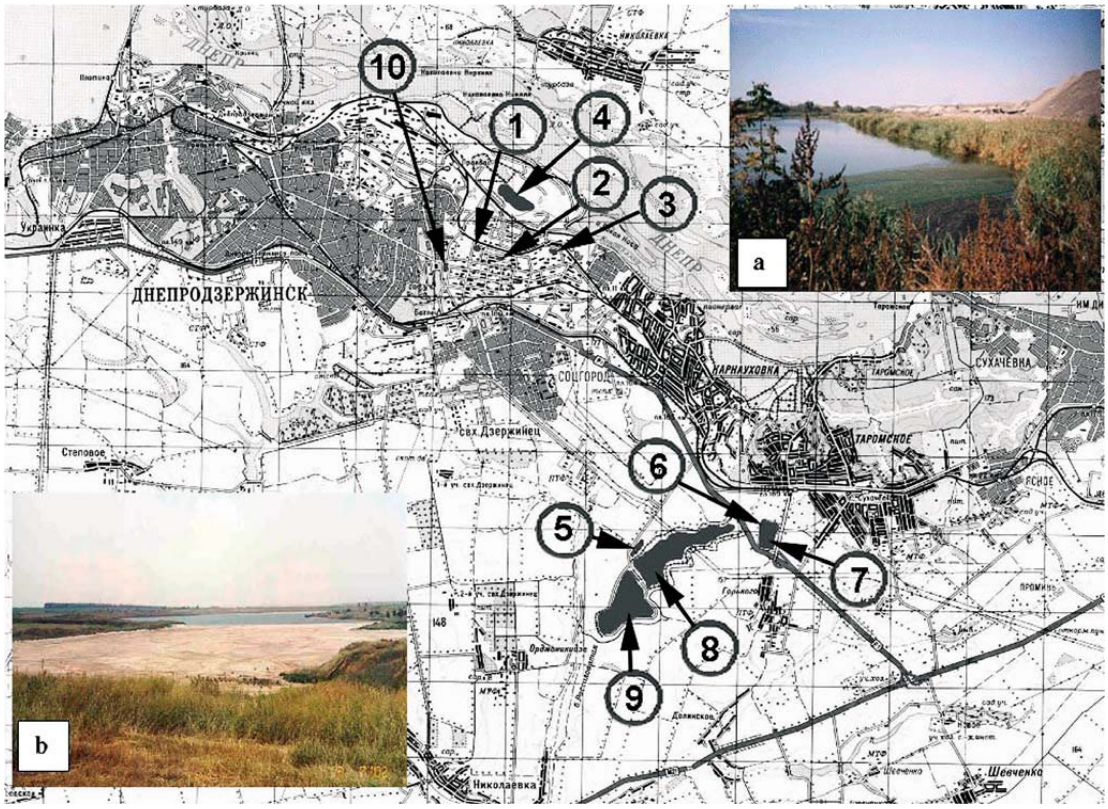

Figure 1 – Location of radioactive waste tailing impoundments within Kamianske (Dnieprodzerzhinsk) city and the region: (a) Dneprovskoye and Konoplianka river, (b) Sukhachevskoye, 1 – Zapadnoye, 2 – Centralny Yar, 3 – Yugo-Vostochnoye, 4 – Dneprovskoye, 5 – Lanthanum Fraction, 6 – Blast Furnace No. 6, 7 – Baza S, 8, 9 – Sukhachevskoye, 1st and 2nd sections, 10 – tailing impoundment in Lazo street

The tailing impoundment located on Lazo street was formed after processing radioactive nitrogen-containing solutions, which were formed at PU PChP, into liquid fertilizers at Dneprodzerzhink Production Union Azot.

Since 1999, experts of the laboratory New Technologies for Processing Raw Materials and Industrial Waste in cooperation with Sorbent Scientific-Pedagogic Centre at Dniprovsk State Technical University (DSTU), have been paying special attention to the issue of radioactive waste handling formed at former PU PChP. These activities include assessment of the possibility to process waste with uranium recovery and bringing them into an environmentally safe condition.

In 2000-2002, a contract was fulfilled with ComPro Inc. (USA) on the comprehensive study of Zapadnoye, Dneprovskoye, and Sukhachevskoye radioactive tailing impoundments [1] in cooperation with Tsvetnye Metaly Research-Technical Centre and SE Ukr R&D Institute for IndTech.

Experts of the laboratory took part in the implementation of project 1160 The Investigation of Level of Environmental Radioactive Contamination in the Sites of Production of the Uranium Concentrate and Elaboration of Recommendations on Affected Territories Rehabilitation (2201 to 2003) funded by Science and Technology Centre in

Ukraine intergovernmental entity. Partially, the results obtained were used when preparing the conclusions of the IAEA experts, who worked within the UNDP-IAEA project aiming to study the condition and impact of uranium mining and processing facilities in Ukraine on water bodies in the Dnieper basin. The technical report and conclusions made by IAEA experts [4] were presented to the Government of Ukraine.

Results were presented [5] on evaluation of the content of natural and man-induced radionuclides ^{238}U, ^{230}Th, ^{226}Ra, ^{210}Pb, ^{232}Th, ^{40}K and ^{137}Cs, gamma-radiation exposure dose rate on the surface of Baza S former uranium ore storage and Sukhachevskoye impoundment (section 2) and comparing results for soil radioactive contamination with physiological parameters of test plant development. The content of movable forms of I-III hazard class elements As; Cd; Pb; Se; Zn; B; Co; Cr; Cu; Ni; Sb; Al; Ba; Mn; Sr; V and accompanying elements Fe, K, Mg, Na, P, Be was assessed [6] in the soil of Baza S uranium ore storage and Sukhachevskoye tailing impoundment. A correlative relationship was found between the concentration of Na, Cd, Be, Ni, B, Co, V, Sr, Zn, Cu movable forms and specific activity of ^{238}U isotope [7].

The maps for time series of the spatial distribution of soil contamination fractions around Sukhachevskoye tailing impoundment are presented [8]. The maps were obtained based on remotely measured hyperspectral satellite images and ground measurements of soil contamination.

Sorption materials are widely used for selective uranium recovery due to their complete insolubility in an aqueous phase, low rate of physical destruction, high sorption and kinetic properties and osmotic stability. For this purpose, organic and inorganic cation and anion exchangers are used as well as materials combining the properties of a selective liquid extractant and a sorbent – solvent impregnated resins and Levextrel-type resins known as Solid Extractants (TVEX) in FSU countries [9]. This paper summarizes research data on the possibility of uranium sorption from radioactive waste of the former PU PChP obtained by the laboratory team.

In cooperation with Radioecological Monitoring Centre (RMC) and DSTU, the data on physical and chemical properties, radionuclide composition of radioactive waste in Zapadnoye tailing impoundment (Figure 2) obtained in 2000 [1] and 2009 [10] were generalized and processed.

Zapadnoye tailing impoundment was in operation during the initial period of the PChP operation since 1949 until 1954. It is located within the II terrace above floodplain of Dnieper River, in used-up clay pit separated by earth-fill dams [1]. The impoundment area is 40 thousand sq. m. The tailing layer thickness varies from 1 m to 12.5 m; the waste total volume is 0.25 million m^3. Chemical composition of waste features basic minerals of uranium ores (quartz, field spar, hydrous micas and kaolinite) as well as reagents used when processing them. The high iron content in tailings is due to processing the slag formed in blast furnace No. 6 of Dneprovsky Integrated Iron and Steel Works. Waste was neutralized before dumping (using lime, ammonia, etc.) resulted in the formation of alkaline conditions (pH=8.5 to 9.5) in tailing materials. Average content in tailings is 1.7 kBq/kg for uranium (238) and 5.9 kBq/kg for radium (226) [11-13].

Figure 2 – Zapadnoye tailing impoundment after erosion-preventive activities

During field works performed by SE Ukr R&D Institute for IndTech, 6 exploratory wells were drilled to a depth of 5.5 m to 19.0 m in 2000 [1] and 8 ones to a depth of 3.0 m to 17.5 m in 2009 within the tailing site contour.

We have demonstrated [10] the conceptual possibility to process radioactive waste accumulated in Zapadnoye tailing impoundment by sorption leaching from pulps using AMP anionite with benzyl pyridinium functional groups (manufactured by Smoly State Enterprise).

A composite sample was used for the study, which was prepared from 7 samples each weighed 100 g. The samples were taken from exploratory wells drilled in 2009.

Radioactive wastes were leached by the mixture contained sulphuric (15 % to 30 %) and nitric (1.5 % to 3 %) acids, reagent grade, at a temperature within 70 °C to 90 °C and phase ratio Solid : Liquid= 1:1-1:2 during 16 hours. The content of uranium isotopes (238, 234) was measured by radiochemical analysis with alpha-spectrometric measurement using Progress-alpha complex with a semiconductor detector (RMC).

It was established that residual acidity after leaching of radioactive wastes sampled at Zapadnoye tailing site was 3.3 to 4.9 times higher than residual acidity after leaching radioactive wastes at Centralny Yar impoundment. This difference was caused probably by the acid-base properties of the tailings associated with different types of processed uranium raw materials and technologies used at workshops No. 2, 22 and 5 of former PU PChP.

We have demonstrated that uranium recovery rate achieved 70 % to 80 % when leaching radioactive waste with the mixture of 15 % sulphuric and 1.5 % nitric acids during 6 hours at a temperature of 70 °C and phase ratio Solid : Liquid = 1:1.

We used the pulp formed after leaching radioactive waste with the mixture of sulphuric 15 % and nitric 1.5 % acid at a temperature of 90 °C and phase ratio Solid : Liquid = 1:1. Uranium was recovered from the pulp cooled up to 60 °C and neutralized by

ammonia solution up to pH = 2.5, in which we put 2 grams of AMP anionite under permanent mixing; the resin was preliminary swollen in distilled water. Uranium concentration was measured by sampling 2 ml of the solution every 2 hours during 8 hours.

It was found that the uranium recovery rate achieved 84 % after 8 hours.

We have estimated [14] the possibility to recover uranium from groundwater accumulated in Centralny Yar tailing impoundment (Figure 3) using AM-p-2 strong-base macroporous anionite based on styrene-divinylbenzene copolymer with 2-hydroxyethyl dimethylammonium functional groups (manufactured by Smoly SE).

Figure 3 – Centralny Yar tailing impoundment

The tailing site was in operation since 1950 until 1954 and located within the gulley. It occupies area 24 thousand sq. m. and contains 130 thousand m^3 of radioactive waste. The waste thickness varies (1 to 2) m to 17.4 m; average thickness is 8.0 m. The waste surface was covered by the fill soil layer (sand clay, sandy soil) of 0.5 m to 3.5 m thick. Average content in tailings is 2.8 kBq/kg for uranium (238) and 60 kBq/kg for radium (226) [11-13, 15].

The tailing site distinctive feature is that the processed pulp was not neutralized; that's why, it is acidic. According to the monitoring data obtained within 2005-2017 [15], the conclusion was made about active uranium leaching from the tailing impoundment body and its ability to migrate into groundwater.

Anionic composition of pore and underground water features sulphate-ion (up to 2.6 g/l SO_4^{2-}) and hydrocarbonate-ion (up to 0.9 g/l HCO_3^-); pH is within 2.5 to 4.0, which promotes uranium to form uranyl anionic complexes.

We assessed the possibility to recover uranium from the tailing site groundwater [14, 16] based on uranium equilibrium distribution between AM-p-2 anionite and uranyl sulphate simulated solution contained sodium sulphate 25 g/l, pH = 1.45 at 20±2 °C. Under these conditions, equilibrium is described with modified Langmuir-Freundlich equation with high determination factor (R^2 = 0.9980):

$$q = \frac{q_m K_{LF} C_e^{n_{LF}}}{1 + K_{LF} C_e^{n_{LF}}}$$

and with the following parameters: maximum capacity q_m is 373.8 mg/g, constant K_{LF} is 8.570×10^{-3} l/mg, empiric factor n_{LF} is 0.7612. C_e is uranium equilibrium concentration, mg/l.

Efficiency of uranium recovery at its content 7 mg/l in pore water and 4 mg/l in underground water [15] was assessed by distribution factor approx. 2 000. Its value allows considering AM-p-2 anionite as an advanced material for uranium recovery from upper ground and underground water of the impoundment.

In cooperation with Ukrainian Hydrometeorological Institute of State Service of Emergencies of Ukraine and National Academy of Sciences of Ukraine, we tested phosphate cationite based on modified plant raw (apricot stone) to recover uranium from radioactively-polluted water accumulated in the basement of building No. 103 (Figure 3) at former PU PChP [17]. Previously, uranium concentrate was purified in this building producing uranium oxide and triuranium octoxide. After the factory forced shutdown in 1992, its territory and buildings were not decontaminated.

Figure 4 – Building No. 103

Today, building No. 103 is rated as extremely contaminated and is among preferential structures for decontamination and further dismantling of polluted hardware and building structures, among all, due to ongoing destruction. Water accumulated in the building basement due to atmospheric precipitation is among factors caused instability of building structures. Rainfall enters rooms and washes out radioactive materials into the basement forming solutions with high uranium content (up to 40 mg/l). That is why it is possible to pump out water from the building only after its decontamination. For this purpose, initial study was carried out regarding the possible use of selective cationite based on modified plant materials.

To perform experiments, water samples were taken from the basement of building No. 103 with its further preservation and acidity correction with 20 % ammonia to

pH = 7. Hydrochemical composition assay confirmed its atmospheric origin (hydrocarbonate-calcium, mineralization up to 0.6 g/l, with low sodium and potassium content 6 mg/l). Up to 90 % of water radioactivity was caused by uranium isotopes (238, 234). Specific activity of U (238, 234) in water was measured using alpha-spectrometric technique with radiochemical pre-treatment at the analytical laboratory of Ukrainian Hydrometeorological Institute. The measurement was made using Alpha Analyst 7200-08 Canberra spectrometer (USA).

We prepared phosphate cationite by alkaline mercerization and phosphorylation using the mixture of phosphoric acid and carbamide. The capacity of the prepared material was measured [17] in batch experiments by contacting 0.5 g of the materials with 0.5 l of aqueous phase during 7 days at room temperature. Uranium specific activity was recomputed into concentration by the ratio activity of 1 g ^{238}U – $1.24 \cdot 10^4$ Bq. Sorption capacity (mg/g) was calculated by the difference of uranium concentration in aqueous phase. The weight of adsorbed uranium was 9.78 mg that means sorption capacity approx. 20 mg/g with distribution factor ~4 800. The results obtained may be proposed as the reasoning for the method and technology intended to decontaminate polluted water before it would be pumped from underground rooms of building No. 103. This cationite may be also used to purify underground water including Dneprovskoye tailing impoundment, in and around which pollution areas that were formed due to migration of chemical components and radionuclides and reached Konoplianka and Dnieper rivers [13, 18].

In cooperation with DSTU, sorption properties were studied for selective uranium recovery from nitric media using solid extractant [19] contained diisooctylmethyl phosphonate (TVEX-DIOMP) with different extractant content. Together with Institute of Organic Chemistry, NAS of Ukraine, and Research Institute of Chemistry, V.N. Karazin Kharkiv National University, we produced impregnate [20] based on porous styrene-divinylbenzene copolymer contained 5,11,17,23-tetrakis-(dipropylphosphinoylmethyl)-25,26,27,28-tetrapropoxycalix[4]arene as active phase and studied its properties regarding selective uranium recovery.

Conclusions. Research data were generalized regarding uranium recovery from radioactive waste formed during operation of Production Union Pridneprovsky Chemical Plant using anionites manufactured by Smoly State Enterprise and the cationite produced from modified natural raw.

It was shown that application of sorption materials is the most expedient and promising method for selective uranium recovery when dealing with remediation of tailings impoundments and handling radioactive wastes of former PU PChP.

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Анотація. Узагальнені результати досліджень щодо можливості сорбційного вилучення урану з радіоактивних відходів виробничого об'єднання «Придніпровський хімічний завод» (ВО «ПХЗ»). Показана принципова можливість вилучення урану методом сорбційного вилуговування з пульп, отриманих у результаті кислотного розкриття радіоактивних відходів хвостосховища «Західне», з використанням аніоніту АМП (ДП «Смоли») з бензилпіридинієвими функціональними групами. При кислотному розкритті відходів сумішшю 15 % сульфатної та 1,5 % азотної кислот вилучення урану в розчин досягає 70-80 %. Застосування сорбційного вилуговування дозволяє додатково вилучити до 15 % урану. Наведені результати оцінки можливості вилучення урану з верхніх ґрунтових і підземних вод хвостосховища «Центральний Яр» з застосуванням сильноосновного макропоруватого аніоніту АМ-п-2 (ДП «Смоли») на основі стирен-дивінілбензольного кополімеру з гидроксиетил-диметиламонієвими функціональними групами. Відмінною рисою хвостосховища є те, що пульпа після переробки практично не зазнала нейтралізації та має кислу реакцію. Хвостосховище створює небезпеку для довкілля завдяки активному вилуговуванню урану з тіла хвостосховища та його здатністю мігрувати у підземні води. Показано, що при концентрації урану в поровій воді 7 мг/дм^3 і підземних водах 4 мг/дм^3 коефіцієнт розподілу може складати ~2000. Наведені результати оцінки вилучення урану фосфорнокислим катіонітом на основі модифікованої рослинної сировини з радіоактивно-забрудненої води підвалу корпусу № 103. Будівля відноситься до надзвичайно забруднених, і э одним з пріоритетних для очищення та наступного демонтажу. Ємність сорбенту по урану, отримана в статичному режимі, склала ~20 мг/г з коефіцієнтом розподілу ~4800. Отримані результати можуть бути запропоновані в якості обґрунтування для створення методу та технології очищення забрудненої води перед її відкачуванням з підвалу будівлі № 103. Виконаний комплекс досліджень показав, що використання сорбційних матеріалів є найбільш доцільним і перспективним для селективного вилучення урану при рішення проблем реабілітації хвостосховищ та поводження з радіоактивними відходами колишнього ВО «ПХЗ».

Ключові слова: Придніпровський хімічний завод, хвостосховище переробки уранових руд, сорбція, аніоніт, катіоніт

Аннотация. Обобщены результаты исследований по возможности сорбционного извлечения урана из радиоактивных отходов производственного объединения «Приднепровский химический завод» (ПО «ПХЗ»). Показана принципиальная возможность извлечения урана методом сорбционного выщелачивания из пульп полученных в результате кислотного вскрытия радиоактивных отходов хвостохранилища «Западное» с использованием анионита АМП (ГП «Смолы») с бензилпиридиниевыми функциональными группами. При кислотном вскрытии отходов смесью 15 % серной и 1,5 % азотной кислот извлечение урана в раствор достигает 70-80 %. Применение сорбционного выщелачивания позволяет дополнительно извлечь до 15 % урана. Приведены результаты оценки возможности извлечения урана из верхних грунтовых и подземных вод хвостохранилища «Центральный Яр» с применением сильноосновного макропористого анионита АМ-п-2 (ГП «Смолы») на основе стирол-дивинилбензольного сополимера с 2-гидроксиэтил-диметиламмониевыми функциональными группами. Отличительной чертой хвостохранилища является то, что пульпа после переработки практически не подвергалась нейтрализации и имеет кислую реакцию. Хвостохранилище создаёт угрозу для окружающей среды из-за активных процессов выщелачивания урана из тела хвостохранилища и его способности мигрировать в грунтовые воды. Показано, что при концентрации урана в поровой воде 7 мг/дм^3 и подземных водах 4 мг/дм^3 коэффициент распределения может составлять ~2000. Приведены результаты оценки извлечения урана фосфорнокислым катионитом на основе модифицированного растительного сырья из радиоактивно-загрязнённой воды подвала корпуса № 103. Здание относится к числу чрезвычайно загрязнённых и является одним из приоритетных для его очистки и последующего демонтажа. Ёмкость сорбента по урану полученная в статическом режиме, составила ~20 мг/г с коэффициентом распределения ~4800. Полученные результаты могут быть предложены в качестве обоснования метода и технологии очистки

загрязнённых вод, которые будут откачиваться из подвальных помещения здания № 103. Выполненный комплекс исследований показал, что использование сорбционных материалов является наиболее целесообразным и перспективным для селективного извлечения урана при решении вопросов реабилитации хвостохранилищ и обращения с радиоактивными отходами бывшего ПО «ПХЗ».

Ключевые слова: Приднепровский химический завод, хвостохранилища переработки урановых руд, сорбция, анионит, катионит

Стаття надійшла до редакції 19.01.2021