UDC 541.49:546.791.6+546.73

DOI: https://doi.org/10.15407/geotm2024.168.061

URANIUM SORPTION FROM THE SOLUTIONS SIMULATED RADIOACTIVELY CONTAMINATED WATER USING SORBENTS OF DIFFERENT ORIGIN

¹Korovin V., ²Pohorielov Yu., ³Cortina J. L., ¹Shestak Yu., ¹Valiaiev O.

¹M.S. Poliakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine ²Dniprovsky State Technical University

Abstract. The paper presents the research results on uranium recovery from the solutions that simulated radioactively contaminated groundwater in the Centralnyi Yar tailings site and the water accumulated in the basement of building No. 103 at the former Production Union Prydniprovsk Chemical Plant using granular ion exchange resins and sorbents produced by modification of vegetal raw materials. Based on the literature data, we selected resins produced by domestic (Smoly JSC) and foreign (Lanxess, Purolite, DuPont) manufacturers and contained guaternary ammonium. benzylpyridinium, carboxylic and iminodiacetic acid functional groups. In addition, the sorption materials based on phosphorylated vegetal material - crushed kernel of apricot Prunus Armeniaca L. and walnut Juglans Regia L. shell were used during the study. Uranium equilibrium distribution between sorbents and simulated solutions was studied in a static mode using the different portion technique by contacting sorbent portions with 20 cm³ of the simulated solution for 24 hours at a temperature of 20±2 °C. Uranium concentration in the aqueous phase was measured by photocolourimetry with the Arsenazo III indicator. As a result of the study, it was found that resins with iminodiacetic acid functionalities featured the highest sorption capacity compared with other ones. The capacity of sorbents made of phosphorylated vegetal materials significantly decreased with the increase of the simulated solution pH. Experimental data on uranium sorption from simulated solutions by granular sorbents and ones made of phosphorylated vegetal raw materials were processed using the Henry equation. It was determined that the uranium distribution factor for granular sorbents decreased in the following sequence when removing it from the solution simulated the groundwater inside the Centralnyi Yar tailing site (cm³/g): Lewatit MDS TP208 (39 450) > Puromet MTA 6002 (16 250) > AM-p (13 880) > Puromet MTS9300 (14 310) > AMP (12 310) > Ambersep 920U (9 006) > AM-p-2 (6 930) > Lewatit MonoPlus M 500 (6 610) > Purolite A530E (3 830) > Purolite C-115 (1 580) > Lewatit CNP-80 (1 110). The values of the uranium distribution factor were 1 635 (AMF) and 1 074 (OMF) for the sorbents based on phosphorylated vegetal materials when removing uranium from the simulated solution with pH = 3.0, and 129 (AMF) and 140 (OMF) for the simulated one with pH = 8.2.

Keywords: uranium, simulated solutions, sorption, granular sorbent, phosphorylated vegetal raw materials.

1. Introduction

Production Union Prydniprovsk Chemical Plant (PCP) was among the first facilities involved in processing various uranium ores and concentrates. During the facility operation (1948–1991), nine radioactive waste tailing sites were formed significantly impacting the environment [1, 2].

Based on the literature data [3], it was defined that migration of radionuclides and chemicals from the tailing facilities, which are located at the former PCP site, contaminate groundwater in the under-surface water-bearing stratum with uranium isotopes (238, 234), cations and anions (sulphate, calcium, magnesium, etc.) typical for the hydrometallurgical processing of uranium ores. Besides, the toxic metal (Mn, Pb, Ni) content significantly exceeded the maximum allowable concentrations for potable water. Discharge of contaminated groundwater into Konoplianka River, a tributary of Dnipro River, resulted in the pollution of the biggest Ukrainian river with toxic chemicals and an increase of uranium isotope concentration.

There are more than 150 buildings and engineering structures [4] within the former PCP site; among them, 28 structures (including buildings No. 103, No. 104 and some others) were directly involved in the processing of uranium-containing ores. A huge amount of fine radioactive materials was accumulated in them. These materials were

³Universitat Politècnica de Catalunya

accumulated in basements and migrated to the adjacent areas due to air flows and atmospheric precipitations that penetrate into the destructing buildings and structures.

Sustainable management of the radioactive waste generated during uranium ore processing requires the development and implementation of effective ways and means to improve environmental safety by applying efficient and affordable recovery methods for uranium compounds and uranium decay elements from dilute aqueous solutions formed during their migration to surface and ground water.

Sorption materials are widely used for selective uranium extraction due to their complete insolubility in the aqueous phase, low physical destruction rate, high sorption and kinetic properties, and osmotic stability.

This research aimed to study uranium sorption from uranium-containing solutions that simulated radioactively contaminated groundwater in the Centralnyi Yar tailing site and the water accumulated in the basement of building No. 103 at the former PCP using granular ion-exchange resins and sorption materials produced by modification of vegetal raw materials.

2. Experimental part

<u>Materials and reagents.</u> We selected granular ion exchange resins with different functionalities, both of domestic (Smoly JSC) and foreign (Lanxess, Purolite, DuPont) manufacturers, based on the literature data on uranium recovery from different media including seawater [5-7]:

- quaternary ammonium: Puromet MTA6002PF [8], Purolite A530E [9], Ambersep 920U [10], AM-p [11], AM-p-2 [12], Lewatit MonoPlus M 500 [13];
 - benzylpyridinium: AMP [14];
 - carboxylic acid: Purolite C115 [15], Lewatit CNP 80 [16];
 - iminodiacetic acid: Lewatit MDS TP 208 [17], Puromet MTS9300 [18].

Additionally, GoPur 3000 [19] was studied; it is a two-in-one polymeric sorbent/flocculant containing amide oxime and hydroxamic functional groups. This material combines the advantages of both inorganic precipitation of metal hydroxides and organic flocculation.

To prepare sorbents based on modified vegetal raw materials, we used crushed kernels of Prunus Armeniaca L apricot (AMF sorbent) and Juglans Regia L. walnut shells (OMF sorbent). The work fraction 1.6 mm to 2.0 mm was sieved using the MLW Thyr 2 laboratory vibrating sieve. Subsequently, the work fraction was mercerized in the 85 g/dm³ NaOH solution for 1 hour in a water bath at a Solid-to-Liquid phase ratio of S:L = 1:1. After mercerization, the materials were washed in distilled water upon attaining pH \approx 7. Then, phosphorylation was carried out with a solution containing 18 % H₃PO₄, 32 % H₂O, and 50 % (NH₂)₂CO: initially, the sorbent portions were soaked in the solution for a day at room temperature, then – at a temperature of \sim 140 °C to 150°C for 4 hours. After cooling, the samples were washed in distilled water to pH \approx 7 and transformed to the H-form with a 5% HCl solution at a Solid-to-Liquid phase ratio of S:L = 1:4 for 24 hours. Finally, the resulting phosphorylated sorbents were washed in distilled water to pH \approx 7 and dried to air-dryness.

The moisture content of the phosphorylated natural sorbents was 10 % for AMF and 14 % for OMF. Total static exchange capacity was 70 mg-eq/g for AMF and 56 mg-eq/g for OMF.

The initial simulated solution was prepared by dissolving uranyl nitrate in distilled water to produce a nitrate solution with a uranium concentration of 500 mg/dm³. Subsequently, we took the required amount of the initial solution and added reagents according to the composition of the radioactively contaminated water, which was defined in [20, 21], and brought it to volume with distilled water. The final simulated solutions had the following composition:

- the solution that simulates the groundwater in the Centralnyi Yar tailing site [20]: U - 15.0 mg/dm³, NO_3^- - 7.81 mg/dm³, $MgCl_2$ - 93.3 mg/dm³, $CaCl_2$ -332 mg/dm³, KCl – 19.1 mg/dm³, MgSO₄ – 1 535 mg/dm³, Na₂SO₄ – 297 mg/dm³, $H_2SO_4 -68.4 \text{ mg/dm}^3$, pH = 3.0;
- the solution that simulated the "basement" water accumulated in building No. 103 at PCP [21]: U – 23 mg/dm³, NO₃⁻ – 12.0 mg/dm³, NaHCO₃ – 387 mg/dm³, CaCl₂ – 83.4 mg/dm^3 , $KCl - 4.60 \text{ mg/dm}^3$, $MgSO_4 - 139 \text{ mg/dm}^3$; pH = 8.2.

Chemicals used during the measurement were at least reagent grade.

Experimental procedure. Uranium equilibrium distribution was studied between the sorbents and simulated solutions by the different portion technique in a static mode by contacting sorbent portions with 20 cm³ of the solution during 24 hours at a temperature of 20±2 °C using the 357-type temperature-adjusted mixer (Elpan, Poland). Solid and liquid phases were separated after sorption.

Analytical procedure. Uranium concentration in the aqueous phase was measured by photocolorimetry [22] with Arsenazo III indicator using a SPEKOL 11 spectrophotocolorimeter in a 10-mm pathway cell at a wavelength of 655 nm. Uranium content in a sorbent was calculated by mass balance.

Moisture weight fraction in the sorbents was measured by drying their portions in the MLW WS 100 drying oven at a temperature of 105 °C to a constant weight and weighing them using the Axis ANG220C analytical laboratory balance.

The total static exchange capacity of the sorbents produced by phosphorylation of vegetal raw materials was measured according to GOST 20255.1-89.

The solution acidity was measured using a combined glass electrode ESC-10603/7 and an OP-211/1 pH meter.

3. Results and discussion

Resin equilibrium capacity (q, mg/g) was calculated by the difference of uranium concentrations in the aqueous phase before and after sorption using the formula:

$$q = \frac{\left(\left[U \right]_{ini} - \left[U \right]_{eq} \right) \cdot V}{m}, \tag{1}$$

where: $[U]_{ini}$ and $[U]_{eq}$ are uranium initial and equilibrium concentrations in the aqueous phase, correspondingly, mg/dm³; V is the simulated solution volume, dm³, m is the resin portion weight on an oven-dry basis.

Table 1 contains the data on uranium recovery with the sorption materials based on phosphorylated vegetal raw materials from simulated solutions with pH values of 3.0 and 8.2.

Table 1 – Uranium capacity for the sorbents based on phosphorylated vegetal feedstock

| Resin weighed portion m, | Moisture content W, % | Solution portion volume V, cm ³ 3 | Uranium initial concentration [U] _{ini} , mg/dm ³ | Uranium equilibrium concentration [U] _{eq} , mg/dm ³ 5 | Capacity q, mg/g | | |
|----------------------------------|---|---|---|--|------------------|--|--|
| 1 | <u> </u> | _ | - | | U | | |
| | Simulated solution with pH = 3.0 | | | | | | |
| 0.0182 | 13.93 | 20 | OMF | 6.89 | 9.21 | | |
| | | | 15.29 | | | | |
| 0.0135 | 13.93 | 20 | 15.29 | 8.49 | 10.07 | | |
| 0.0075 | 0.0075 13.93 20 15.29 11.10 11.21 | | | | | | |
| 0.0177 | 10.01 | 20 | AMF | 7 .00 | 10.50 | | |
| 0.0175 | 10.01 | 20 | 15.29 | 5.88 | 10.73 | | |
| 0.0131 | 10.01 | 20 | 15.29 | 8.01 | 11.09 | | |
| 0.0079 | 10.01 | 20 | 15.29 | 9.37 | 14.95 | | |
| Simulated solution with pH = 8.2 | | | | | | | |
| OMF | | | | | | | |
| 0.0510 | 13.93 | 20 | 24.02 | 17.36 | 2.61 | | |
| 0.0357 | 13.93 | 20 | 24.02 | 18.62 | 3.02 | | |
| 0.0276 | 13.93 | 20 | 24.30 | 20.53 | 2.73 | | |
| AMF | | | | | | | |
| 0.0536 | 10.01 | 20 | 24.02 | 16.51 | 2.80 | | |
| 0.0359 | 10.01 | 20 | 24.02 | 20.01 | 2.23 | | |
| 0.0189 | 10.01 | 20 | 24.02 | 21.80 | 2.34 | | |

Experimental data demonstrated a significant decrease in the capacity of the phosphorylated vegetal feedstock when increasing the simulated solution pH. Such a change in capacity was also noted [20] for the phosphorylated cellulose-based sorbents; it was caused, probably, by the formation of poorly recovered uranium complexes [20].

Table 2 presents the results of uranium recovery by ion exchange resins and GoPur3000 sorbent/flocculant.

Table 2 – Uranium capacity for granular sorbents when recovering from the simulated solution with pH=3.0

| Resin weighed | | Solution portion | | Uranium equilibrium | Capacity | |
|---|---------|--------------------|----------------------------------|---------------------------------|----------|--|
| portion | content | volume | concentration | concentration | q, mg/g | |
| <i>m</i> , g | W, % | V, cm ³ | $[U]_{ini}$, mg/dm ³ | $[U]_{eq}$, mg/dm ³ | q, mg/g | |
| 1 | 2 | 3 | 4 | 5 | 6 | |
| Sorbents with quaternary ammonium functionalities | | | | | | |
| Puromet MTA 6002 PF | | | | | | |
| 0.0148 | 39.10 | 20 | 13.47 | 0.80 | 17.12 | |
| 0.0102 | 39.10 | 20 | 13.47 | 1.11 | 24.17 | |
| 0.0060 | 39.10 | 20 | 13.47 | 2.51 | 36.74 | |

continuation of table 2

| | | | | continuation | n of table 2 |
|--------|-------|--------------------|----------------|---|--------------|
| 1 | 2 | 3 | 4 | 5 | 6 |
| | | Am | bersep 920U | | |
| 0.0111 | 53.47 | 20 | 13.47 | 1.54 | 21.46 |
| 0.0077 | 53.47 | 20 | 13.47 | 2.23 | 29.10 |
| 0.0047 | 53.47 | 20 | 13.47 | 4.80 | 36.56 |
| | | Pu | rolite A-530 | | |
| 0.0106 | 46.50 | 20 | 14.22 | 4.62 | 18.04 |
| 0.0079 | 46.50 | 20 | 14.22 | 5.61 | 21.77 |
| 0.0042 | 46.50 | 20 | 14.22 | 7.96 | 30.04 |
| | - 1 | Lewatit | MonoPlus M-500 | | |
| 0.0143 | 38.93 | 20 | 15.80 | 2.49 | 18.62 |
| 0.0101 | 38.93 | 20 | 15.80 | 3.67 | 23.93 |
| 0.0062 | 38.93 | 20 | 15.80 | 5.25 | 33.87 |
| | | l | AM-p-2 | | l |
| 0.0106 | 56.77 | 20 | 13.47 | 2.10 | 21.48 |
| 0.0074 | 56.77 | 20 | 13.47 | 3.28 | 27.58 |
| 0.0045 | 56.77 | 20 | 13.47 | 5.76 | 34.64 |
| 0.00.0 | 00177 | | AM-p | | |
| 0.0105 | 48.12 | 20 | 15.50 | 0.88 | 27.78 |
| 0.0078 | 48.12 | 20 | 15.50 | 1.79 | 35.23 |
| 0.0039 | 48.12 | 20 | 15.50 | 4.52 | 55.68 |
| | | orbents with benz | | | |
| | | | AMP | | |
| 0.0116 | 42.34 | 20 | 15.50 | 1.60 | 23.87 |
| 0.0085 | 42.34 | 20 | 15.50 | 2.25 | 31.28 |
| 0.0047 | 42.34 | 20 | 15.50 | 4.18 | 47.89 |
| 0.0017 | | Sorbents with car | | | 17.05 |
| | | | rolite C-115 | A COLIGINATION OF THE PARTY OF | |
| 0.0096 | 52.84 | 20 | 14.22 | 7.51 | 13.95 |
| 0.0071 | 52.84 | 20 | 14.22 | 8.74 | 15.39 |
| 0.0039 | 52.84 | 20 | 14.22 | 11.28 | 15.25 |
| 0.0057 | 32.01 | • | vatit CNP-80 | 11.20 | 13.23 |
| 0.0112 | 44.62 | 20 | 14.22 | 8.51 | 10.22 |
| 0.0081 | 44.62 | 20 | 14.22 | 9.57 | 11.42 |
| 0.0045 | 44.62 | 20 | 14.22 | 11.58 | 11.63 |
| 0.0043 | | Sorbent with iming | | | 11.03 |
| | | | it MDS TP 208 | otionarries . | |
| 0.0092 | 53.10 | 20 | 15.50 | 0.54 | 32.55 |
| 0.0092 | 53.10 | 20 | 15.50 | 0.88 | 42.14 |
| 0.0038 | 53.10 | 20 | 15.50 | 1.99 | 72.03 |
| 0.0036 | 33.10 | | net MTS 9300 | 1.77 | 12.03 |
| 0.0100 | 50.91 | 20 | 14.22 | 1.07 | 26.40 |
| 0.0100 | 50.91 | 20 | 14.22 | 1.72 | 33.97 |
| 0.0074 | 50.91 | 20 | 14.22 | 4.22 | 53.66 |
| | | | | hydroxamic functionalil | |
| 0.0092 | | | | | |
| | 10.08 | 20 | 14.22 | 10.21 | 8.76 |
| 0.0067 | 10.08 | 20 | 14.22 | 10.52 | 10.98 |
| 0.0038 | 10.08 | 20 | 14.22 | 12.15 | 10.99 |

The data showed that the sorbents with iminodiacetatic acid functionalities featured a higher capacity as compared with other ion exchange resins. GoPur 3000 has not removed uranium from the simulated solution with a high pH value (8.2).

We have not tested granular sorbents for uranium recovery from the model solution with pH = 8.2 since it is not economically feasible to use expensive granular resins to treat small values of the water accumulated in the basement of buildings.

Experimental data on uranium recovery from simulated solutions by different sorbents were processed with a Henry equation that describes sorption at low equilibrium concentrations of the recovered component most adequately [23]:

$$q = K_H \cdot |U_{eq}| , \qquad (2)$$

where: q is the sorbent equilibrium capacity, mg/g, $[U_{eq}]$ is uranium equilibrium concentration, mg/dm³, K_H is Henry constant, dm³/g.

We used OriginPro 2016 software (demo-version) to fit experimental data and to calculate Henry equation coefficients.

Processing results are given in Table 3, which contains Henry isotherm parameters (Henry constant, dm^3/g , determination factor R^2) as well as uranium distribution factor (K_d , cm^3/g), which was calculated based on the Henry constant.

Table 3 – Henry isotherm parameters and uranium distribution factor

| Sorbent | Equation | \mathbb{R}^2 | K _d , cm ³ /g | | | |
|---|----------------------------|----------------|-------------------------------------|--|--|--|
| Simulated solution with pH=3.0 | | | | | | |
| Sorbents with quaternary ammonium functionalities | | | | | | |
| Puromet MTA 6002 PF | $q = 16.25 \cdot [U_{eq}]$ | 0.968 | 16 250 | | | |
| Ambersep 920U | $q = 9.01 \cdot [U_{eq}]$ | 0.931 | 9 010 | | | |
| Purolite A-530 | $q = 3.83 \cdot [U_{eq}]$ | 0.999 | 3 830 | | | |
| Lewatit MonoPlus M-500 | $q = 6.61 \cdot [U_{eq}]$ | 0.997 | 6 610 | | | |
| AM-p-2 | $q = 6.93 \cdot [U_{eq}]$ | 0.959 | 6 930 | | | |
| AM-p | $q = 13.88 \cdot [U_{eq}]$ | 0.922 | 13 880 | | | |
| Sorbents with benzylpyridinium functionalities | | | | | | |
| AMP | $q = 12.31 \cdot [U_{eq}]$ | | 12 310 | | | |
| Sorbents with carboxylic acid functionalities | | | | | | |
| Purolite C115 | $q = 1.58 \cdot [U_{eq}]$ | 0.980 | 1 580 | | | |
| Lewatit CNP 80 | $q = 1.11 \cdot [U_{eq}]$ | 0.993 | 1 110 | | | |
| Sorbent with iminodiacetic acid functionalities | | | | | | |
| Lewatit MDS TP 208 | $q = 39.45 \cdot [U_{eq}]$ | 0.972 | 39 450 | | | |
| Puromet MTS9300 | $q = 14.31 \cdot [U_{eq}]$ | 0.946 | 14 310 | | | |
| GoPur3000 sorbent/flocculant | | | | | | |
| GoPur 3000 | $q = 0.93 \cdot [U_{eq}]$ | 0.994 | 930 | | | |
| Phosphorylated vegetal raw sorbents | | | | | | |
| AMF | $q = 1.57 \cdot [U_{eq}]$ | 0.990 | 1 570 | | | |
| OMF | $q = 1.13 \cdot [U_{eq}]$ | 0.987 | 1 130 | | | |
| Simulated solution with pH=8.2 | | | | | | |
| AMF | $q = 0.12 \cdot [U_{eq}]$ | 0.9586 | 120 | | | |
| OMF | $q = 0.15 \cdot [U_{eq}]$ | 0.993 | 150 | | | |

According to the research performed, uranium distribution factor decreased within the following sequence for granular ion exchange resins when recovering it from the simulated solution with pH = $3.0 \text{ (cm}^3/\text{g)}$: Lewatit MDS TP208 (39 450) > Puromet MTA 6002 (16 250) > AM-p (13 880) > Puromet MTS 9300 (14 310) > AMP (12 310) > Ambersep 920U (9 010) > AM-p-2 (6 930) > Lewatit MonoPlus M 500 (6 610) > Purolite A530E (3 830) > Purolite C-115 (1 580) > Lewatit CNP-80 (1 110) > GoPur 3000 (930) (Figure 1).

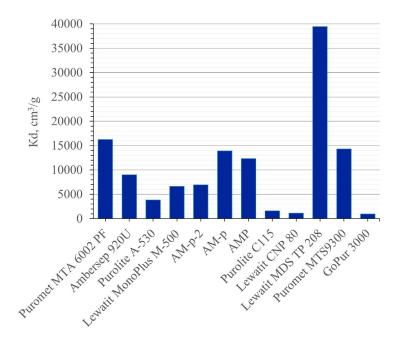


Figure 1 – Uranium distribution factor during its recovery by various sorbents from the solution that simulates underground water in the body of the Centralnyi Yar tailing site

The distribution factor for AM-p-2 resin correlated with the one that has been calculated for the system AM-p-2 – uranyl sulphate simulated solution with uranium concentration 4 mg/dm³ to 7 mg/dm³ [25, 26].

For the sorption materials produced by the vegetal feedstock phosphorylation, the uranium distribution factor was 1 570 (AMF) and 1 130 (OMF) when recovering uranium from the simulated solution with pH = 3.0 and 120 (AMF) and 150 (OMF) – for the simulated solution with pH = 8.2. These values correlated with the total static exchange capacity of these materials.

4. Conclusions.

Based on the experimental results, it was found that ion exchange resins with iminodiacetic acid functionalities recovered uranium the best from the solution, which simulated radioactively contaminated groundwater formed in the Centralnyi Yar tailing site at the former Production Union PCP (distribution factor was 14 310 cm³/g and 39 450 cm³/g depending upon the resin brand). At the same time, resins with carboxylic acid resins demonstrated the worst sorption (1 110 cm³/g and 1 580 cm³/g, respectively). The distribution factor for nitrogen-containing adsorbents changed from 3 830 cm³/g to 16 250 cm³/g. For the phosphorylated sorbents based on

crushed apricot kernels (AMF) and walnut shells (OMF), the distribution factor was 1 570 cm³/g and 1 130 cm³/g, correspondingly, close to the values featured for ion exchange resins with carboxylic acid functionalities.

Distribution factor decreased to 120 cm³/g (AMF) and 150 cm³/g (OMF) for the phosphorylated vegetal materials during uranium recovery from the solution that simulated radioactively-contaminated water accumulated in the basement of building No. 103.

The work was done within research project DR 0122U001317.

REFERENCES

- 1. Korovin, V., Korovin, Yu., Laszkiewicz, G., Lee, O., Shmatkov, G., Koshik, Yu., Semenets, G. and Merkulov, V. (2001), "Problem of radioactive pollution as a result of uranium ores processing", *Scientific and Technical Aspects of International Cooperation in Chornobyl*, Slavutych, Ukraine, 2001, pp. 461–468. https://inis.iaea.org/collection/NCLCollectionStore/_Public/34/023/34023916.pdf?r=1&r=1.
- 2. Shmatkov, G., Korovin, V., Koshik, Yu., Ryaboshapka, S. and Shestak, Yu. (2001), "Radioactive contamination of city territory due to work of uranium processing plant and the ways of its solution", Proc. 10th International Symposium Loss Prevention and Safety Promotion in the Process Industries, Stokholm, Sweden, 19–21 June 2001, vol. 2, pp. 1215–1223. https://doi.org/10.1016/B978-044450699-3/50036-7.
- 3. Bugai, D.O., Zanoz, B.Yu., Lavrova, T.V., Korychensky, K.O., Kubko, Yu.I., Avila, R. and Rets, Yu.M. (2021), "Development of the groundwater monitoring system in the zone of influence of uranium production legacy facilities of the Prydniprovsky Chemical Plant", *Geologičnij žurnal*, issue 4, pp. 56–70. https://doi.org/10.30836/igs.1025-6814.2021.4.240111
- 4. Tkachenko, Yu. (2020), Prydneprovskiy Khimichnyi Zavod uranova spadschyna Ukrainy. Ogliadova dopovid pro istoriu diyalnosti ta suchasniy stan kolyshniogo vyrobnychogo obednannia Prydneprovskiy Khimichnyi Zavod [Prydniprovsky Chemical Plant Ukraine's uranium heritage. Overview report on the history and current state of the former production association Prydniprovsky Chemical Plant], Bellona Foundation, Oslo, Norway. https://network.bellona.org/content/uploads/sites/3/2020/11/Pridniprovsky-Chemical-plant-Ukrainian.pdf.
- 5. Smedley, P.L., and Kinniburgh, D.G. (2023), "Uranium in natural waters and the environment: Distribution, speciation and impact", *Applied Geochemistry*, vol. 148, 105534. https://doi.org/10.1016/j.apgeochem.2022.105534.
- 6. Gibert, O., Valderrama, C., Peterkóva, M., and Cortina, J.L. (2010), "Evaluation of selective sorbents for the extraction of valuable metal ions (Cs, Rb, Li, U) from reverse osmosis rejected brine", *Solvent Ext. Ion Exch.*, vol. 28, pp. 543–562. https://doi.org/10.1080/07366299.2010.480931.
- 7. Petersková, M., Valderrama, C., Gibert, O., and Cortina, J.L. (2011) "Extraction of valuable metal ions (Cs, Rb, Li, U) from reverse osmosis concentrate using selective sorbents", *Desalination*, vol. 286, pp. 316-323. https://doi.org/10.1016/j.desal.2011.11.042.
- 8. Production data sheet. Puromet MTA6002PF (2024), available at: https://www.purolite.com/product-pdf/MTA6002PF.pdf (Accessed 17 April 2024).
- 9. Production data sheet. Purolite A 530E (2024), available at: https://www.purolite.com/product-pdf/A530E.pdf (Accessed 17 April 2024).
- 10. Production data sheet. DuPont™ AmberSep™ 920U SO4 Ion Exchange Resin (2023), available at: https://www.dupont.com/content/dam/dupont/amer/us/en/water-solutions/public/documents/en/IER-AmberSep-920U-SO4-PDS-45-D00801-en.pdf (Accessed 17 April 2024).
- 11. Strongly basic macroporous anionite AM-p (2021), available at: http://smoly.com.ua/silnoosnovnyie-makroporistyie-1 (Accessed 17 April 2024).
- 12. Korovin, V., Valiaiev, O., Zontov, O., Zontova, L., Pilchyk, V. and Pysmenniy B. (2019), "Uranium (VI) sorption from sulphuric solutions by AM-p-2 anionite", *Essays of Mining Science and Practice 2019*, E3S Web of Conferences 109, 00039. https://doi.org/10.1051/e3sconf/201910900039.
- 13. Production information. Lewatit MonoPlus M500 (2011), available at: https://www.lenntech.com/Data-sheets/Lewatit-MonoPlus-M-500-L.pdf (Accessed 17 April 2024).
 - 14. Strongly basic AMP anionite (2021), available at: http://smoly.com.ua/silnoosnovnyiy-anionit-amp (Accessed 19 April 2024).
- 15. Production data sheet. Purolite C 115 (2015), available at: https://www.lenntech.com/Data-sheets/Purolite-C115E-L.pdf (Accessed 17 April 2024).
- 16. Production information. Lewatit CNP 80 (2020), available at: https://www.lenntech.com/Data-sheets/Lewatit-CNP-80-EN-L.pdf (Accessed 17 April 2024).
- 17. Lewatit MDS TP 208 (2022), available at: https://lanxess.com/en-US/Products-and-Brands/Products/l/LEWATIT--MDS-TP-208 (Accessed 19 April 2024).
- 18. Production data sheet. Puromet MTS9300 (2024), available at: https://www.purolite.com/product-pdf/MTS9300.pdf (Accessed 19 April 2024).
 - 19. GoPur 3000 Organisches Polymeraggregat zur Abtrennung von Uran aus Bergbauwässern (2017), available at:

https://www.hego-biotec.com/wp-content/uploads/2021/05/22-Pb-GoPur-3000.pdf (Accessed 22 April 2024).

- 20. Korychenskyi, K.O., Laptev, G.V., Voitsekhovich, O.V., Lavrova, T.V. and Dyvak, T.I. (2018), "Speciation and mobility of uranium in tailings materials at the U-production legacy site in Ukraine", *Nuclear Physics and Atomic Energy, vol.* 19, issue 3, pp. 270–279. http://doi.org/10.15407/jnpae2018.03.270.
- 21. Valyaev, A.M., Korovin, V.Yu. and Lavrova, T.V. (2018), "Radioactive contaminated water treatment using phosphoric cation-exchange based on modified vegetable raw material", XXV Shchorichna Naukova Konferentsiia Instytutu ladernykh Doslidzhen NAN Ukrainy [XXV Annual Scientific Conference of the Institute for Nuclear Research of the National Academy of Sciences of Ukraine, 16–20 April 2018, pp. 207–208. https://inis.iaea.org/search/search.aspx?orig_q=RN:49075908.
- 22. Muhammad, Sally Sayed. (2020), "Uranium sorption using Lewatit MonoPlus M500 from sulphate media", *Science Journal of Chemistry*, vol. 8(1), pp. 7–19. https://doi.org/10.11648/j.sjc.20200801.12.
- 23. Bykov, T.A. (2011) "Sorption of radionuclides from aurous media with modified natural materials", Ph.D. Thesis, Radiochemistry, RAS Institute of Physical Chemistry and Electrochemistry, Moscow, Russia.
- 24. Korovin V., Pohorielov Yu., Shestak, Yu., Valiaiev, O. and Cortina, J.L. (2021), "Rhenium recovery from sulfuric media using AMR anionite", *Essays of Mining Science and Practice 2021,* IOP Conference Series: Earth and Environmental Science, 970, 012009. https://doi.org/10.1088/1755-1315/970/1/012009.
- 25. Korovin, V.Yu., Valiaiev, A.M., Zontrol, A.V. and Zontova, L.V. (2019), "Assessment of the possibility to recover uranium (VI) by AM-p-2 anionite from groundwater of Centralnyi Yar tailing facility", XXVI hchorichna Naukova Konferentsiia Instytutu ladernykh Doslidzhen NAN Ukrainy [XXV Annual Scientific Conference of the Institute for Nuclear Research of the National Academy of Sciences of Ukraine], Kyiv, Ukraine, 8–12 April 2019, pp. 176–177. https://inis.iaea.org/search/searchsinglerecord.aspx?recordsFor=SingleRecord&RN=50056629.
- 26. Korovin V.Yu., Valiaiev O.M., Pohorielov, Yu.M., Shestak, Yu.G., Lavrova T.V. and Haneklaus, N. (2021), "Uranium sorption from radioactive waste of uranium ore processing at Pridneprovsk Chemical Plant", *Geo-Technical Mechanics*, no. 157, pp. 212–222. https://doi.org/10.15407/geotm2021.157.212.

About the authors

Korovin Vadym, Candidate of Chemical Sciences (Ph.D.), Head of Laboratory of New Technologies for Raw and Industrial Waste Processing, Department of Elastomeric Component Mechanics in Mining Machines, M.S. Poliakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine (IGTM of the NAS of Ukraine), Dnipro, Ukraine, sorbent2005@ukr.net, ORCID **0000-0003-1247-5292**.

Pohorielov Yurii, Senior Researcher at Sorbent Scientific and Pedagogic Center, Dniprovsk State Technical University State Higher Education Institution (DGTU SHEI), Kamianske, Ukraine, yura50 11 08@ukr.net, ORCID **0000-0003-2069-1243**.

Cortina Jose Luis, Ph.D. (Applied Chemical Sciences), Professor in Chemical Engineering, Barcelona East Engineering School, Universitat Politècnica de Catalunya, Barcelona, Spain, jose.luis.cortina@upc.edu, ORCID 0000-0002-3719-5118.

Shestak Yurii, Senior Engineer at the Laboratory of New Technologies for Raw and Industrial Waste Processing, Department of Elastomeric Component Mechanics in Mining Machines, M.S. Poliakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine (IGTM of the NAS of Ukraine), Dnipro, Ukraine, <u>or-numiz@ukr.net</u>, ORCID **0000-0003-1446-8782**.

Valiaiev Oleksandr, Engineer at the Laboratory of New Technologies for Raw and Industrial Waste Processing, Department of Elastomeric Component Mechanics in Mining Machines, M.S. Poliakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine (IGTM of the NAS of Ukraine), Dnipro, Ukraine, alexandr.valyaev@gmail.com, ORCID 0000-0001-9882-059X.

ДОСЛІДЖЕННЯ СОРБЦІЇ УРАНУ З РОЗЧИНІВ, ЩО МОДЕЛЮЮТЬ РАДІОАКТИВНО ЗАБРУДНЕНІ ВОДИ, СОРБЕНТАМИ РІЗНОГО ПОХОДЖЕННЯ

Коровін В., Погорєлов Ю., Кортіна Х., Шестак Ю., Валяєв О.

Анотація. В роботі наведені результати дослідження сорбційного вилучення урану з уранвмісних розчинів, що моделюють радіоактивно забруднені підземні води хвостосховища «Центральний Яр» та підвальні води будівлі № 103 колишнього ВО «ПХЗ», гранульованими сорбентами та сорбційними матеріалами на основі модифікованої рослинної сировини. На основі літературних даних для дослідження були відібрані гранульовані іонообмінні смоли вітчизняного (АТ «Смоли») та закордонного виробництва (Lanxess, Purolite, DuPont) з четвертинними амонієвими, бензилпіридінієвими, карбоксильними та імінодіацетатними функціональними групами. Крім того, для дослідження були використані сорбенти на основі фосфорильованої рослинної сировини - подрібнену кісточку абрикоса *Prunus Armeniaca L*. та шкарлупу горіха волоського *Juglans Regia L*. Рівноважний розподіл урану між сорбентами та розчинами, що моделюють радіоактивні води, вивчали в статичному режимі методом різних наважок шляхом контактування сорбенту з 20 см³ розчину протягом 24 годин при температурі 20±2 °C. Концентрацію урану у водній фазі вимірювали фотоколориметричним методом з індикатором арсеназо ІІІ. Визначено, що сорбент з імінодіацетатними групами мають найбільшу ємність, ніж інші іонообмінні смоли. Ємність сорбентів на основі модифікованої рослинної сировини суттєво знижується зі збільшенням рН модельного розчину. Експериментальні дані щодо сорбції урану з модельних розчинів гранульованими

сорбентами та матеріалами на основі фосфорильованої рослинної сировини були оброблені рівнянням Генрі. Визначено, що коефіцієнт розподілу урану для гранульованих сорбентів знижується у наступній послідовності при його вилученні з розчину, що моделює води, утворювані у тілі хвостосховища «Центральний Яр» (см 3 /г): Lewatit MDS TP208 (39450) > Puromet MTA 6002 (16250) > AM- π (13880) > Puromet MTS9300 (14310) > AM π (12310) > Ambersep 920U (9010) > AM- π -2 (6930) > Lewatit MonoPlus M 500 (6610) > Purolite A530E (3830) > Purolite C-115 (1580) > Lewatit CNP-80 (1110) > GoPur 3000 (930). Для сорбентів на основі фосфорильованої сировини значення коефіцієнту розподілу урану складали 1570 (АМФ) та 1230 (ОМФ) при вилученні урану з модельного розчину з pH=3,0 та 120 (АМФ) і 150 (ОМФ) для модельного розчину з pH=8,2.

Ключові слова: уран, модельні розчини, сорбція, гранульовані сорбенти, фосфорильована рослинна сировина.