



## Studies on uranium recovery from a U-bearing Radoniów Dump

Katarzyna Kiegiel ,  
Otton Roubinek ,  
Dorota Gajda ,  
Paweł Kalbarczyk ,  
Grażyna Zakrzewska-Kołtuniewicz ,  
Andrzej G. Chmielewski

**Abstract.** This work reports the possibility of uranium recovery from a post-mining uranium ore dump in Poland by a bioleaching method. The studies were conducted on the dump leaching model with the mass of 570 kg of uranium bearing mineral material from Radoniów pile and in the periodic bioreactor with a work volume of 80 dm<sup>3</sup> and with mechanical mixing and aeration of the charge. The uranium concentration in the examined material was about 800 ppm. In this process, the consortium of microorganisms isolated from former mines was used. It was composed of the following microorganisms: *Bacillus*, *Pseudomonas*, *Sphingomonas*, *Thiobacillus*, *Halothiobacillus*, *Thiomonas*, and *Geothrix*. The efficiency of the uranium bioleaching process was 98% in the reactor, and a yield of 70% was obtained in the dump leaching model. The post-leaching solution contained significant amounts of uranium ions that were separated in two stages: (1) by ion chromatography and then (2) by a two-step precipitation method. The resulting solution was a source of ammonium diuranate, the precursor of yellowcake (uranium oxides).

**Keywords:** Ammonium diuranate precipitation • Bioleaching • Uranium

K. Kiegiel✉, D. Gajda, P. Kalbarczyk,  
G. Zakrzewska-Kołtuniewicz, A. G. Chmielewski  
Institute of Nuclear Chemistry and Technology  
Dorodna 16 Str., 03-195 Warsaw, Poland  
E-mail: k.kiegiel@ichtj.waw.pl

O. Roubinek  
Institute of Nuclear Chemistry and Technology  
Dorodna 16 Str., 03-195 Warsaw, Poland  
and Warsaw University of Technology  
Faculty of Chemistry  
Laboratory of Technological Processes  
Noakowskiego 3 Str., 00-664 Warsaw, Poland

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### Introduction

Nuclear energy continues to play an important role in today's energy sector, and according to all forecasts, it will remain a significant component of the energy mix in the future. This is connected with a need of decarbonization of the energy sector, which still needs development of a sustainable energy source. Nuclear power can fill the gap left after shutdown of power plants using fossil fuels such as lignite and hard coal. For this reason, the continuous development of nuclear energy leads to an inevitable increase in the demand for nuclear fuel and thus uranium. It is expected that future world demand for uranium will be covered by exploitation of secondary resources such as low-grade ore bodies and industrial wastes [1, 2]. In addition to the well-developed methods that are already applied for uranium recovery [3, 4], bioleaching of uranium from raw materials and industrial waste containing uranium might be also a technically available solution [5–7]. Bioleaching is an economically advantageous process that is broadly used for the recovery of metals from various materials [8, 9]. In this study, the post-mining uranium dump from Radoniów (Fig. 1) was considered as the potential



**Fig. 1.** The photo of a material sampling point at the post-mining uranium dump in Radoniów.

secondary resource of uranium. The Radoniów deposit is located in Western Sudetes (SW Poland). Uranium mining had been started in there in 1954 and continued until 1960.

One of the most important steps in U fuel manufacturing is obtaining the yellowcake. The yellowcake can be precipitated from the solution over a wide pH range, either in acidic or alkaline media. It depends on the composition of the solution and precipitant. The precipitation of uranium salt from acidic solution is carried out by adding reagents such as aqueous ammonia, sodium hydroxide, magnesium oxide, or hydrogen peroxide [10, 11].

### Materials and methods

Post-mining U-bearing dumps are located near the former Radoniów mine. Currently, two dumps exist there, the so-called Small Dump and Big Dump – they differ in size and uranium content. The material investigated in this study originated from the Small Dump and the uranium concentration was about 747–800 ppm. The chemical analysis of two samples of the ore from that pile is presented in Table 1. About 1.5 tons of material were collected from the pile (in two portions) and then pre-fractionated.

The consortium of microorganisms isolated from former mines was used for bioleaching. It was composed of the following microorganisms: *Bacillus*, *Pseudomonas*, *Sphingomonas*, *Thiobacillus*, *Halothiobacillus*, *Thiomonas*, and *Geothrix* [7, 12]. The chemical composition of the bacteria medium is listed in Table 2.

All reagents were of analytical grade and were used as received without further purification. Dowex 1 × 8 resins were supplied by Dow Chemi-

**Table 2.** The composition of K0 bacteria medium used in the bioleaching process

Component	Concentration (g/dm <sup>3</sup> )
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	5
KCl	0.166
KH <sub>2</sub> PO <sub>4</sub>	0.083
MgSO <sub>4</sub> · 7H <sub>2</sub> O	0.830
Ca(NO <sub>3</sub> ) <sub>2</sub>	0.024
pH 2	

cal Company. The total content of uranium in the post-bioleaching solution was determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis [13].

### Results and discussion

#### Treatment of uranium ores

The studies were carried out in the periodic bioreactor with agitation and aeration of the charge and in the model of dump leaching with the mass of 570 kg of uranium-bearing mineral material from Radoniów pile. The uranium concentration in the examined material was about 750–800 ppm (Table 1).

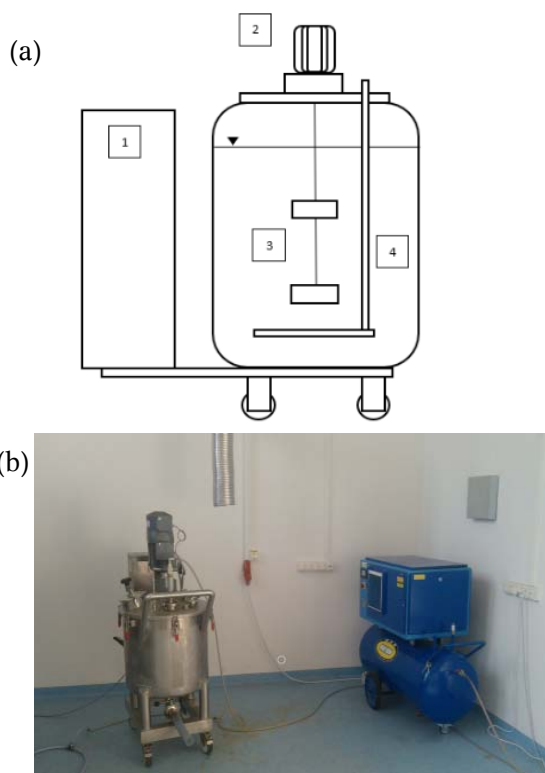
Bioleaching of uranium ores was carried out in the bioreactor developed at the Institute of Nuclear Chemistry and manufactured by Bocard Kates sp. z o. o. from Olsztyn, Poland. The capacity of the bioreactor was 100 dm<sup>3</sup>. The bioreactor was equipped with temperature and pH control systems, as well as with a mixing system with speed control and an aeration device. Figure 2 shows the scheme and photos of the reactor and the test stand.

In the experiment, about 98% of uranium was leached after 51 days of the process. The results are presented in Fig. 3.

In the second test, the experiment was scaled up, and bioleaching was carried out in the fixed-bed deposit to simulate *in situ* heap leaching process. The bed dimensions were 100 cm × 120 cm × 24 cm. The deposit was placed in a pallet box as shown in Fig. 4. The pallet box was set up in such a way that it allowed free drainage of the liquid (slope at an angle of 2° related to the outlet from the box). The construction of the bed deposit was as follows: a stainless steel mesh was placed in the box, and on top of it, a layer of pieces of ore with dimensions of more than 5 cm was placed. The height of this layer was 6–7 cm. On top of this layer, the material with a grain size less than 5 cm was placed. The mass of charge was 570 kg. Leaching was performed for 120 days. During the process, sulfuric acid was added to the solution to maintain the pH at ~2. The efficiency of uranium leaching reached 70%.

**Table 1.** Chemical analysis of samples taken from the Small Dump in Radoniów

U	Th	Cu	Co	Mn	Zn	La	V	Yb	Mo	Ni	Sb	Fe
(ppm)												
747	12	12	21	291	58	24	47	3	3	27	5	23 200
801	14	14	18	369	100	29	52	3	5	23	7	25 200

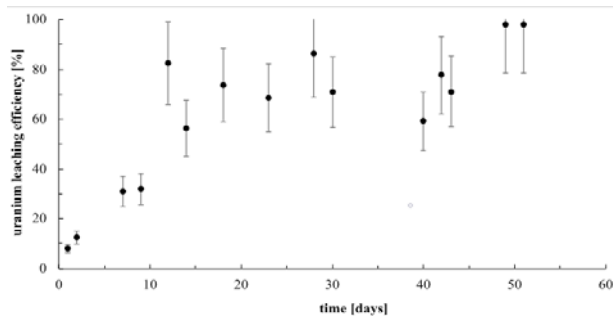


**Fig. 2.** (a) The scheme of the reactor: 1 – double-Rushton mixer, 2 – bubbler, 3 – control cabinet, and 4 – engine; (b) the reactor and control system panel built by Kates sp. z o. o.

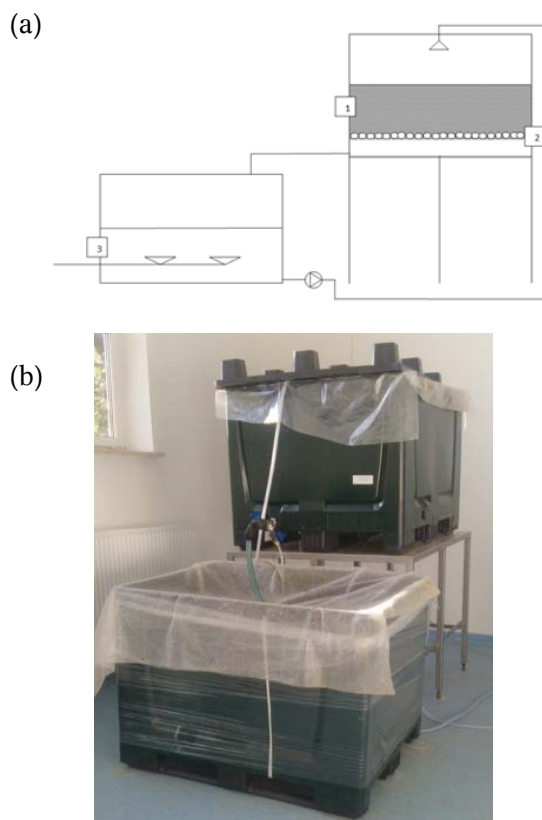
Aeration was carried out by two disc diffusers in the lower tank. The solution was pumped into the spraying system located above the bed in the upper container. Liquid samples were collected at the inlet and outlet of the container. As shown in Fig. 5, the uranium concentration increased over time and reached a maximum after 120 days, and then, it started to decrease.

**Ion-exchange chromatography**

After bioleaching uranium from the low U-content Radoniów ore, ion-exchange (IX) chromatography was used to separate uranium from other accompanying metals. The Dowex 1 × 8 (200–400 mesh) anion exchanger was chosen for this process. IX column parameters were as follows: H resin = 18.3 cm,



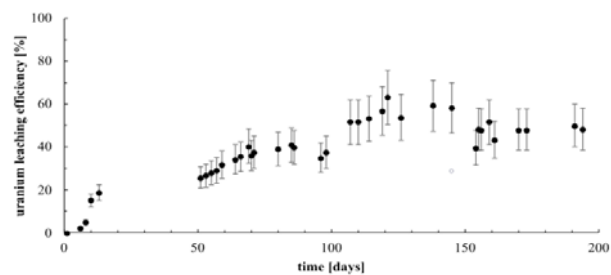
**Fig. 3.** The efficiency of uranium bioleaching in the reactor (initial uranium concentration in the rock: 750–800 ppm).



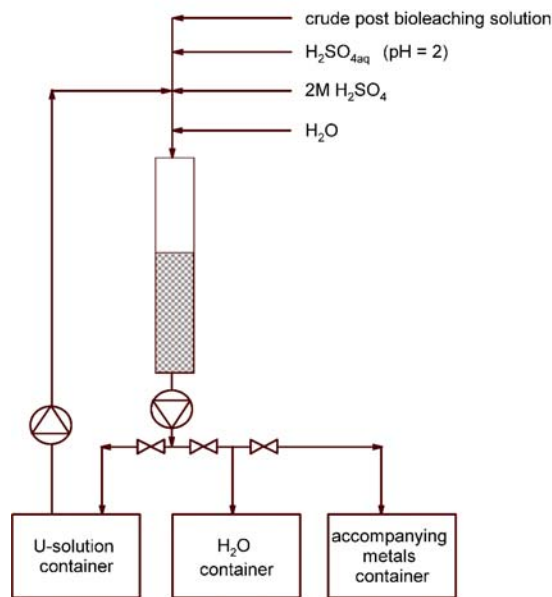
**Fig. 4.** Fixed-bed reactor. (a) The scheme of the experimental stand: 1 – leaching solution, 2 – U-bearing rocks from Radoniów pile, and 3 – post-leaching solution. (b) The experimental rig photo.

$D = 3.92 \text{ cm}$ ,  $V \text{ resin} = 221 \text{ cm}^3$ , effluent flow =  $7.77 \text{ cm}^3/\text{min}$ .

The post-bioleaching solution ( $700 \text{ cm}^3$ ) was introduced into the IX column (Fig. 6). Subsequently,  $3000 \text{ cm}^3$  of  $\text{H}_2\text{SO}_{4\text{aq}}$  ( $\text{pH} = 2$ ) was used to rinse the accompanying metal ions, e.g., Fe, rare earth elements (REE), etc. They were collected in an accompanying metal container. Uranium ions, adsorbed on the resin bed, were eluted with 2M sulfuric acid, and this solution was collected into a “U solution container”. In the first rinsing cycle of uranium, only fresh 2M  $\text{H}_2\text{SO}_4$  was used. Each subsequent aliquot of the eluting solution was composed of 2M  $\text{H}_2\text{SO}_4$  solution from the “U solution container” and fresh 2M  $\text{H}_2\text{SO}_4$ , in the ratio of  $900 \text{ cm}^3 : 300 \text{ cm}^3$ . At this stage, the uranium concentration was done (Table 3). The analysis of samples after I, X, XIV, and XVII cycles was also performed.



**Fig. 5.** The effect of time on uranium bioleaching in fixed-bed deposit (initial uranium concentration in the rock: 750–800 ppm).



**Fig. 6.** The scheme of ion exchange process, used for the purification uranium post-bioleaching solution.

**Table 3.** The degree of uranium concentration by IX chromatography in the sample after bioleaching

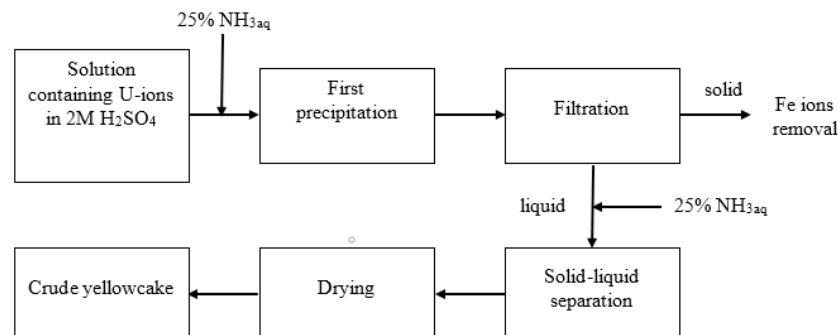
Sample	Cycle no.	U (ppm)	Uranium concentration degree
U-1	I	272	–
U-2	X	327	1.20
U-3	XIV	375	1.38
U-4	XVIII	413	1.52

The U-4 samples from the XVIIIth cycle were used to precipitate the yellowcake.

In the process of uranium bioleaching, significant amounts of iron ions were co-leached. Unfortunately, these ions did not separate completely in the IX column. The U-4 solution after IX chromatography contained about 85 ppm of iron, which impedes precipitation of uranium salts. For that reason, the pretreatment of the U-4 solution was needed before final precipitation of U salts.

### Yellowcake precipitation

The aim of the preliminary study was to select precipitating agents and reaction conditions appropriate



**Fig. 7.** Two-step precipitation of ammonium diuranate from prior purified post-bioleaching solution.

for the recovery of uranium. Based on preliminary studies [14], the precipitation of uranium as ammonium diuranate was chosen. Ammonium diuranate can be easily transformed into uranium oxide (U<sub>3</sub>O<sub>8</sub>) by calcination at 750°C for 4 h. This method allows us to obtain a pure product from the solution with a low concentration of uranium. It was found that the efficiency of the model solution was 84–95% for the concentration ranging between 0.3 mg/cm<sup>3</sup> and 2.4 mg/cm<sup>3</sup>.

The obtained solution contained iron ions, and for that reason, two-stage precipitation was adopted (Fig. 7).

Samples with a volume of 300 cm<sup>3</sup> were used for the precipitation process. In the first step of precipitation, iron ions were removed from the solution using 25% NH<sub>3aq</sub>. U solution (in 2M H<sub>2</sub>SO<sub>4</sub>) was heated up to 60°C in a 600 cm<sup>3</sup> beaker on the magnetic agitator with heating. After that, the ammonia solution was added dropwise to obtain a pH of 4–5. Subsequently, the whole mixture was agitated at 60°C for 1 h. Then, the obtained suspension was filtered, without cooling it, with a sintered disc filter funnel (G5).

The filtered U solution was heated again up to 60°C. After that, the ammonia solution was added after the first crystals formed (pH 8–10). The obtained mixture was heated for 4 h at 60°C and slowly agitated (~70–100 rpm). After that, the suspension was cooled over the night. On the next day, the solution was separated from precipitated U salts. The solid residue was dried at 60°C for 6–7 h and then at 105°C for 1 h. After that, the solid residue was weighed, dissolved in HNO<sub>3</sub>, and subjected to ICP-MS analysis to identify the purity of the obtained solid phase. Ammonium diuranate with a yield of 60% was obtained, and iron separation from U was carried out with a yield of 99%.

### Conclusion

The objective set by the circular economy policy requires that the recovery of metals from industrial waste should be considered in the context of environmental protection and saving natural resources.

Studies incumbently performed at the Institute of Nuclear Chemistry and Technology (INCT) have proven the possibility of bioleaching processes' application for metal extraction from post-mining uranium dumps. The obtained 70% efficiency



of uranium bioleaching in fixed-bed deposit is a very promising result. Bioleaching efficiency and the process rate observed in a stirred reactor were higher; however, the energy consumption was rather high, which makes the process less economical. The outcomes of the study are developed analytical procedures and methods of dump leaching on a pilot scale, as well as a method of uranium separation from the solution obtained from bioleaching. The post-bioleaching solution contained significant amounts of iron ions that were separated in two stages: by IX chromatography and then by two-stage precipitation. The resulting solution was a source of ammonium diuranate, which is the precursor of uranium oxide purified from iron ions with an efficiency of 99%. The yellowcake was precipitated with a yield of 60%.

The obtained results are a collection of base guidelines for the preparation of technical assumptions for the design a bioleaching installation for the processing of 30 tons of charge on a dump. The resulting technology can be implemented to extract uranium from post-mining dumps in the future.

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## ORCID

A. G. Chmielewski  <http://orcid.org/0000-0001-6262-5952>  
 D. Gajda  <http://orcid.org/0000-0002-6335-4792>  
 P. Kalbarczyk  <http://orcid.org/0000-0003-4264-3410>  
 K. Kiegiel  <http://orcid.org/0000-0003-2624-7303>  
 O. Roubinek  <http://orcid.org/0000-0002-6492-7118>  
 G. Zakrzewska-Kołtuniewicz  <http://orcid.org/0000-0001-5201-1551>

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