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A COMPARISON OF URANIUM RECOVERY FROM LOW-GRADE ORE BY BIOLEACHING AND ACID LEACHING

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Abstract: The objective of this work was to compare the bioleaching with the acid leaching of uranium under similar process conditions within 65 days. The low-grade uranium ore used in the experiments was collected from Radoniów's 'small' dump, Poland. Bioleaching and acid leaching studies were carried out in identical columns. The isolated bacterial consortium from the Radoniów's mine was used for the bioleaching process. A solution of sulphuric acid and H_2O_2 as oxidizing agent was used for the acid leaching. The extraction of uranium under acid leaching conditions reached maximum of 64 ± 13 % w/w after 31 days. The bioleaching of uranium achieved a maximum extraction of 75 ± 15 % w/w after 55 days. In this study an attempt was made to demonstrate the relationship between the shrinking-core model and the experimental data by plotting the fractional conversion of uranium against time.

Keywords: *bioleaching, acid leaching, column leaching, low-grade ore, uranium, recovery, shrinking core model*

Introduction

Acid leaching and bioleaching of uranium have been investigated in numerous studies (Abzalov, 2012; Abhilash and Pandey, 2013; Aslam and Aslam, 1970; Bhargava et al., 2015; Bosecker, 1997; Gajda et al., 2015; Hamidian, 2011; Frackiewicz et al., 2012; Mishra et al., 1997; Mishra et al., 2009; Muñoz et al., 1993; Rewerski et al., 2013; Wawszczak et al., 2014; Qui et al., 2011). However, there are few reports regarding the comparison of these leaching methods for the same material and process conditions. Therefore, studies on the possibility of indigenous uranium resources are being carried out. Leaching is an established and relatively successful method of metal extraction, especially from high-grade ores (Abzalov, 2012). However, in the Polish case the most resources are low-grade ores (Gajda et al., 2015; Frackiewicz et al., 2012).

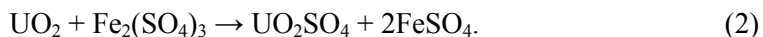
Uranium ores in Poland contain about 250–1100 mg·kg⁻¹ U. Soils of Poland contain average amounts of U of 1.6 mg·kg⁻¹ (lowland) and up to >10 mg·kg⁻¹ in the mountain soils (Sudety Mountains). The Radoniow mine is one of the largest uranium deposits exploited in Poland (Rewerski et al., 2013). In the Radoniow waste case, dump bioleaching recovery can reach 60% of uranium content, batch reactor bioleaching 80%, and packed column about 70%. The most profitable process due to maintenance cost is dump bioleaching (Drewniak, 2014). The previously study reported recovery of U, Cu, Zn, Co, Ni and rare metals (La, Yb) as well (Piestrzynski et al., 1996). Percolation bioleaching using Radoniow's waste can reach 75±22% of uranium recovery. During bioleaching of uranium, also other metals (including rare metals) recovery was reported (Drewniak, 2014). The economy of uranium recovery from these ores is rather low. Bioleaching techniques could be economic on an industrial scale only when using material containing above 0.03% U₃O₈ (Rewerski et al., 2013). A better situation may be foreseen when uranium is a by-product in the hydrometallurgical recovery of other metals (Wawszczak et al., 2014).

Biotechnology has potential for applications in the mining industry (Baranska and Sadowski, 2013; Mishra et al., 1997). Preliminary results show that material deposited in dumps may be useful for biotechnological processes. Bioleaching is a useful method of waste utilization and low-grade ores exploitation (Rewerski et al., 2013).

Uranium can be released from sulfide minerals by direct and indirect bioleaching (Bosecker, 1997). In direct bioleaching, there is physical contact between the bacterial cell and the mineral sulfide surface. In indirect mechanism, the microorganisms need not be in direct contact with ore surface. In bacterial leaching of uranium ores, the tetravalent uranium (insoluble) is oxidized to its hexavalent state (soluble). The ferric ion actually oxidizes uranium, while the oxidizing agent oxidizes ferrous ion to ferric ion. More details are given by Bosecker (1997). Therefore, the uranium oxidation state and iron speciation are crucial to interpret the bioleaching process (Baranska and Sadowski, 2013; Gajda et al., 2015). The direct bioleaching of uranium can be described according to reaction (1) (Abhilash et al., 2015):



In general, the indirect bioleaching of uranium from uranium ores occurs according to the reaction (2) (Bosecker, 1997):



The main microorganisms used in bacterial leaching processes belong to the genus *Acidithiobacillus*, *Leptospirillum* and *Sulfobacillus*. Other microorganisms including heterotrophs, fungi (e.g. *Penicillium* species) and yeasts (e.g. *Rhodotorula* species) (Rewerski et al., 2013) are useful in this process. All earlier mentioned microorganisms show high tolerance to uranyl ions and heavy metals (Munoz et al., 1995).

Acidithiobacillus ferrooxidans is one of the most widely employed microorganisms in the bioleaching process (Baranska and Sadowski, 2013).

Many factors, such as aeration rate, pH, temperature, resistance of microorganisms to metal ions, type of microorganisms, particle size, shape of solids, redox potential and degree of mixing play important roles in uranium extraction. Ore alteration plays an important role in the recovery of uranium (high efficiency with a short period of leaching time). However, the temperature, pH and oxygen concentration in the leaching solution play the key role in leaching processes as well (Munoz et al., 1993; Bosecker, 1997; Abhilash and Pandey, 2013). Microorganisms can improve selective dissolution of metals by penetrating into the molecular structure of the materials, breaking existing chemical and mechanical bonds, consequently forming free ions or new compounds (Bhargava et al., 2015).

Acid leaching has been applied mainly in large operations (Bhargava et al., 2015). Acid leaching is highly selective, and uranium recovery range from 70% to 90% is possible. However, bioleaching methods may be applied to small operations as well. In the acid leaching, a 40-70% pore volume in the material is required, while in bio-recovery a bigger pore volume is required (Abhilash and Pandey, 2013). Bioleaching efficiency is generally high, typically reaching 50-98%. In this process, common materials and simple equipment can be used. The emission of vapour products, for instance, the sulphuric acid in the acid leaching are possible, even in acid leaching done in reactors off-gases are always collected and treated. Therefore, bioleaching methods can be considered as environmentally friendly, because emission of gaseous pollutants are not observed (Abhilash and Pandey, 2013).

The following techniques can be applied at an industrial scale in bioleaching: dump leaching, heap leaching, in situ leaching, vat leaching, percolation leaching, mine waters biotransformation, and stirred tank bioleaching. The choice of method is influenced by the grade, depth, shape, size and thickness of the ore deposits, as well as other parameters (Hamidian, 2011). The known industrial applications of waste and uranium ores are based on heap leaching, dump leaching, percolation leaching, mine waters biotransformation (Chmielewski et al., 2016; Rewerski et al., 2013).

The goal of the present study was to compare uranium recovery by bioleaching and acid leaching in identical columns under similar process conditions for the same material.

Materials and methods

Mineralogical characterization of ore

Uranium mining in Lower Silesian Voivodeship of Poland was carried out from 1954 until 1960. The mined uranium ores explored in the Lower Silesia region were polymetallic. The ores contained pitchblende, uraninite, autunite, metaautunite, uranocircite, torbernite, metatorbernite, uranophane, sklodowskite, gummite, fourmarierite and libiegite (Piestrzynski et al., 1996).

The Radoniów mine is one of the largest uranium deposits exploited in Poland. This deposit is located in the northern part of the Iżera Metamorphic Complex, Gmina (the principal unit of administrative division of Poland as 'commune') Lubomierz, Lower Silesian Voivodeship, Poland (Jaskolski, 1967a; Jaskolski, 1967b; Kaczmarek, 1959). Two waste dumps, designated 'small' and 'large', are located in the vicinity of the Radoniów village (Rewerski et al., 2013). In the present study, the low-grade uranium ore used for column leaching tests was mined from Radoniów's 'small' dump. The Radoniów ore deposit is a hydrothermal, gneiss-hosted stockwork, composed fluorite veinlets with quartz, pitchblende and iron hydroxides and contained a rather poor assemblage of accompanying sulfides. The uranium mineralization type of dumps is in stockworks and pipes cutting gneisses (Domanska-Siuda, 2010; Jaskolski, 1967a; Jaskolski, 1967b; Kaczmarek, 1959).

The chemical leaching and bioleaching processes conduce the presence of pyrite as well as relatively low pH (<6.0) (Rewerski et al., 2013). Radoniów's ore contains pyrite. It is important because bioleaching process is carried out in the presence of pyrite and in acid conditions (Drewniak, 2014). Mineralogical characterization of Radoniów's dumps ('small' and 'large') is the following: autunite ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12(\text{H}_2\text{O})$), elaterite (a variety of bitumen), galena (PbS), goethite ($\text{Fe}^{3+}\text{O}(\text{OH})$), gummite (a mixture of: boltwoodite $(\text{K},\text{Na})(\text{UO}_2)(\text{SiO}_3\text{OH}) \cdot 1.5\text{H}_2\text{O}$, clarkeite $(\text{Na},\text{Ca},\text{Pb})(\text{UO}_2)\text{O}(\text{OH}) \cdot 0.1\text{H}_2\text{O}$, curite $\text{Pb}_3(\text{UO}_2)_8\text{O}_8(\text{OH})_6 \cdot 3\text{H}_2\text{O}$, kasolite $\text{Pb}(\text{UO}_2)[\text{SiO}_4] \cdot \text{H}_2\text{O}$, soddyite $(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$, uraninite UO_2 , uranophane $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}$), hematite Fe_2O_3 , marcasite FeS_2 , metaautunite (intermediate member of metaautunite $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{--}8\text{H}_2\text{O}$ – chernikovite $(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ – metaankoleite $\text{K}_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ solid solution), metauranocircite $(\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O})$, Mn-oxides (MnO , Mn_3O_4 , Mn_2O_3 , MnO_2 , Mn_2O_7), pitchblende (UO_2), pyrite (FeS_2), torbernite $(\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O})$, uranocircite $(\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O})$, uranopilite $((\text{UO}_2)_6(\text{SO}_4)\text{O}_2(\text{OH})_6 \cdot 14\text{H}_2\text{O})$ (Domanska-Siuda, 2010; Eastaugh et al., 2008; Jaskolski, 1967a; Jaskolski, 1967b; Kaczmarek, 1959; <http://www.mindat.org>).

Chemical characteristics of ore

In materials deposited in the Radoniów 'small' and 'large' dumps (the pH of materials 5.8–6.0) the uranium ($306\text{--}801 \text{ mg}\cdot\text{kg}^{-1}$) and iron ($18700\text{--}25200 \text{ mg}\cdot\text{kg}^{-1}$) concentrations as well as the level of emitted radiation dose are relatively high. Dose rate in materials (screening measure of surface layer) deposited in dumps ($1.5\text{--}4.4 \mu\text{Sv}\cdot\text{h}^{-1}$) is about eight times higher than annual radiation dose limit for non-radiation workers and general public in Poland (Drewniak, 2014).

Samples representing the material taken from Radoniów's 'small' dump were selected. This ore can be considered as representative for whole dump. Sieving was used for determining particle-size distribution in uranium ore samples that were selected for our leaching experiments. The sieve shaker with the standard sieve set

VEB Metallweberei NEUSTADT/ORLA (aperture sizes: 10 mm, 2.5 mm, 0.5 mm) was used for the ore classification. Representative ore fractions are shown in Fig. 1.



Fig. 1. Representative ore fractions before leaching. (A) 10–20 mm, (B) 2.5–10 mm, (C) 0.5–2.5 mm

The concentration of uranium and accompanying elements were determined by inductively coupled plasma mass spectrometry (ICP-MS) technique according to the procedure described by (Chajduk et al., 2013). We assumed that initial metals content of Radoniów's 'small' dump ore is average content of three ore fractions: 10–20 mm ($714.5 \pm 35.7 \text{ mg} \cdot \text{kg}^{-1}$), 2.5–10 mm ($445.6 \pm 22.3 \text{ mg} \cdot \text{kg}^{-1}$) and 0.5–2.5 mm ($576.2 \pm 28.8 \text{ mg} \cdot \text{kg}^{-1}$). Therefore, the initial uranium content of ore samples that were selected for our leaching experiments was $578.8 \pm 86.0 \text{ mg} \cdot \text{kg}^{-1} \text{ U}$ (average of all fractions).

The content of selected metals in uranium ore samples that were picked for our experiments are presented in Table 1.

Table 1. Average content of selected metals in Radoniów's ore in $\text{mg} \cdot \text{kg}^{-1}$

Deposit notation	U	Th	Cu	Co	La	V	Yb	Fe
Radoniów 'small' dump	578.8	10.8	13.3	9.6	35.5	61.7	3.6	29813.5

Inoculum preparation

The Faculty of Biology (University of Warsaw, Poland) has isolated and developed 25 microbial consortia able to oxidize iron under both neutral and acidic conditions (Rewerski et al., 2013). Microbial consortia were isolated from dumps wastes in Kopaniec, Kromnow, Grzmiaca, and the Radoniów 'small' and 'large' dumps. First, genetic and biotechnological studies for each isolated consortia carried out. Indigenous microorganisms living in dump material can extract metals both neutral and acid conditions were proved. Based on the metagenomic studies of DNA isolated from earlier mentioned dumps it was confirmed that there exist bacteria able to siderophore production, e.g. *Bacillus*, *Pseudomonas*, *Sphingomonas*, and bacteria able to oxidize inorganic sulphur compounds, e.g. *Thiobacillus*, *Halothiobacillus*, *Thiomonas*, *Geothrix* (Rewerski et al., 2013).

The microorganisms isolated from the Radoniow mine were used in the bioleaching of uranium ore. Culture adaptation was performed in a mechanically agitated bioreactor at 24.5 °C, pH = 2.5, $pO_2 = 119.5\%$ (oxygen saturation level) and 100 rpm stirrer rotating speed. The bacterial consortium was grown in 9K nutrient medium for 10 days. This medium containing $30 \text{ g}\cdot\text{dm}^{-3}$ $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, $5 \text{ g}\cdot\text{dm}^{-3}$ $(\text{NH}_4)_2\text{SO}_4$, $0.166 \text{ g}\cdot\text{dm}^{-3}$ KCl, $0.083 \text{ g}\cdot\text{dm}^{-3}$ KH_2PO_4 , $0.830 \text{ g}\cdot\text{dm}^{-3}$ $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$, $0.024 \text{ g}\cdot\text{dm}^{-3}$ $\text{Ca}(\text{NO}_3)_2$ was developed by (Silverman and Lundgren, 1959). This medium was prepared from analytical grade chemicals and distilled water. The inoculum contained $1.24\cdot 10^7$ cells cm^{-3} calculated in a Thoma counting chamber after staining.

Methods of measurement and analysis

The ICP–MS method (inductively coupled plasma mass spectrometry; spectrometer model ELAN DRC II, Perkin Elmer) was used for the qualitative and quantitative analyses of the metal contents in leaching and post-leaching liquid samples, with high sensitivity and precision. The limit of detection for uranium is $23 \text{ ng}\cdot\text{cm}^{-3}$. The procedure of ICP–MS technique was described by (Chajduk et al., 2013). The liquid samples for analysis were taken from the recirculation flasks (Fig. 2). The pH and temperature of the leaching slurries were measured at room temperature using the multifunction meter CX-105 Elmetron IP67 with a pH electrode. The oxygen concentration in solutions was measured using the multifunction meter CX-105 Elmetron IP67 with the oxygen gas electrode.

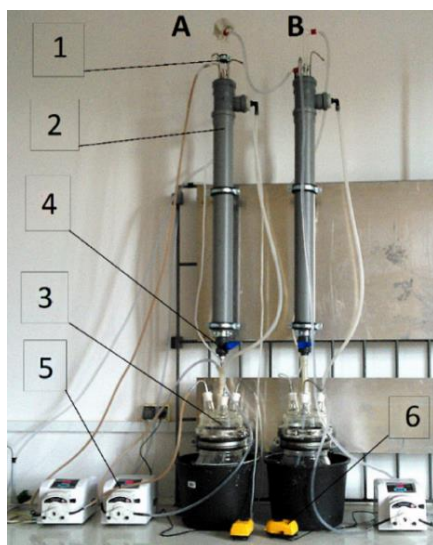


Fig. 2. Installations used for the bioleaching (A, aerated leaching solution) and the acid leaching of uranium ore (B, non-aerated leaching solution). (1) Liebig condenser; (2) Packed column; (3) Round-bottomed flask; (4) Shut-off valve; (5) Peristaltic pump; (6) Aeration pump

Percolation columns

The experiments were carried out with about 3 kg ore in columns (bioleaching – 2939 g, acid leaching – 2967 g). Packing of these columns were divided into three different size fractions: 0.5–2.5 mm 34% w/w, 2.5–10 mm 57% w/w, 10–20 mm 9% w/w. The ore packing mode in the both columns is presented in Fig. 3. This ore packing mode prevented the fall of fine particles from top to bottom during both experiments in columns.

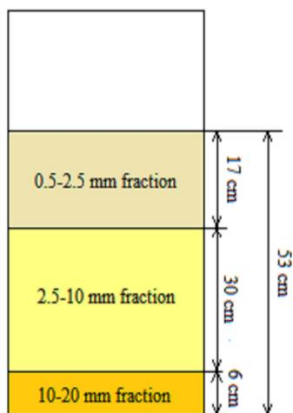


Fig. 3. The ore packing mode in both columns

Both types of leaching experiments were performed in polyvinyl chloride (PVC) columns: 7 cm internal diameter (D) and 90 cm height (H), H/D ratio about 13 (Fig. 2). In percolation leaching the ratio of the internal diameter of the column (D) to the particle size of ore (d) is significant. The ratio $D/d > 7$ must be established (Abhilash and Pandey, 2013) to avoid the solution running down along the walls of the column. In both cases, in bottom of columns filter plates were used to avoid the passage of fine particles. A constant level of liquids was established in the bottom of columns by means of syphon systems. In both cases, the Liebig condensers were placed at the top of columns in order to prevent loss of the leaching solution due to evaporation (Fig. 2).

Both columns were fed with the leaching solution using peristaltic laboratory pump (BT-300EA with head 153YX, Aqua-Trend). The leaching solution was passed through the ore packing by gravity. In the next step, leaching liquid was recirculated through a side loop with a peristaltic pump. A total of 5 dm³ of the leaching solution was recirculated in both cases.

Process comparisons

The acid leaching process with the addition of the oxidizing agent was examined. In the present work 30% w/v of H₂O₂ (analytical grade, POCH, Poland) was used

as an oxidizing agent. This solution is most commonly available, non-toxic and relatively cheap (Abhilash and Pandey, 2013). In the acid leaching of uranium and other metals from the Polish Peribaltic sandstones major differences in effectiveness of oxidizing agents (MnO_2 , KMnO_4 , H_2O_2 , KClO_3) were not noted (Gajda et al., 2015). Both experiments were conducted at room temperature, and the pH of the feed was maintained at 1.93-2.05. The loss of volume due to sampling of the leaching solution was maintained by adding OK medium containing 5 g dm^{-3} $(\text{NH}_4)_2\text{SO}_4$, 0.166 g dm^{-3} KCl , 0.083 g dm^{-3} KH_2PO_4 , 0.830 g dm^{-3} $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.024 g dm^{-3} $\text{Ca}(\text{NO}_3)_2$ (Silverman and Lundgren, 1959). This medium was prepared from analytical-grade chemicals and distilled water. The optimum pH for the bioleaching of uranium in the presence of the bacterial consortium was 2.0.

The leaching solution was passed through the ore packing by gravity and with a peristaltic pump that generated a negative pressure to induce the solution flow. This pump sucked the liquid from the bottom of the column. In the bioleaching and the acid leaching solution flow rates were $0.04\text{-}0.05 \text{ dm}^3 \cdot \text{h}^{-1}$ and $1.48\text{-}9.10 \text{ dm}^3 \cdot \text{h}^{-1}$, respectively. The differences between the two columns were due to a lower flow rate in the bioleaching column than the acid leaching, probably caused by the changes in the ore's porosity during the experiments. Only in the bioleaching air was injected above packing in the column and in the flask continuously at $1.3 \text{ dm}^3 \cdot \text{min}^{-1}$. The leaching solutions were re-circulated for 5 hours per day. The ore packing in columns was regularly flooded for 19 hours per day. The total metal extract is significantly higher in the flooded mode than in the non-flooded mode (Munoz et al., 1995). Several papers (Aslam K. and Aslam M., 1970) have demonstrated that daily irrigation is more effective than weekly in the presence of bacteria. In the industry the irrigation frequency is determined, for instance, by the rate of evaporation and the concentration of the uranium in the liquid phase efflux. Generally, the irrigation rate depends on the ore's permeability. Other significant conditions during the experiments in packed columns were temperature and oxygen concentration in the leaching liquid. The temperatures of acid and bioleaching solutions were in the range $20\text{-}29^\circ\text{C}$. The oxygen concentration ranges of acid and bioleaching solutions were $2.40\text{-}5.32 \text{ mg dm}^{-3}$ and $3.13\text{-}5.91 \text{ mg dm}^{-3}$, respectively. In the bioleaching process, 2 dm^3 of bacterial consortium and 3 dm^3 of OK medium solution were fed at the rate of $2.182 \text{ dm}^3 \cdot \text{h}^{-1}$. In the acid leaching process, the solution of $2.5 \text{ M H}_2\text{SO}_4$ (diluted H_2SO_4 , min. 95% analytical grade, POCH, Poland) at $\text{pH} = 2.0$ was fed at the rate of $2.182\text{-}10.008 \text{ dm}^3 \cdot \text{h}^{-1}$. The bioleaching solution (above the packing in the column and in the flask) was aerated continuously using the aeration pump (Air Fish 2 W, Aqua Szut). It was important to ensure oxygen availability for the microorganisms.

Results and discussion

Uranium extraction

The uranium extraction, R , was calculated in the following way (Gajda et al., 2015):

$$R = \frac{m}{m_o} \cdot 100 \% \quad (3)$$

where: m is the total mass of uranium analyzed from the post-leaching solution (g); m_o is the total mass of uranium in the raw material before experiments (g).

The leaching results for bioleaching and acid leaching processes are presented in Table 2. The recorded dissolution of uranium in acid leaching conditions reached a maximum value of $64 \pm 13\%$ w/w after 31 days. In the bioleaching of uranium case, a maximum of $75 \pm 15\%$ w/w recovery after 55 days was achieved. We obtained similar effectiveness of uranium in percolator bioleaching as in the previous study of (Drewniak, 2014). The measurement uncertainty of initial uranium content ($\text{mg} \cdot \text{kg}^{-1}$) and maximum uranium recovery ($\text{g} \cdot \text{dm}^{-3}$, % w/w) shown in Table 2 are calculated using the exact differential method (Bures et al., 1967).

Table 2. The leaching results

Process	Radoniow ‘small’ dump ore	Maximum U content (in post-leaching solution)	
	U content in ore, $\text{mg} \cdot \text{kg}^{-1}$	g dm^{-3}	% w/w
Bioleaching	578.8 ± 86.0	0.254 ± 0.038	75 ± 15
Acid leaching		0.219 ± 0.033	64 ± 13

Kinetic models of uranium recovery

A general analytical equation has been taken from the previous work (Hunter, 2013) to describe the kinetic parameters of the leaching processes in columns. The kinetic two-parameter and non-linear equation that describes the uranium recovery as a function of the leaching time is the following (Hunter, 2013):

$$R = 100 \cdot (1 - \exp(-a \cdot t^b)) \quad (4)$$

where: R is the extraction (%), t is the leaching time (days), and the a and b parameters are constants. The coefficients (a , b) in the kinetic models (Table 3) were estimated with a Gauss-Newton method using the StatSoft Statistica Version 10.

Table 3. Coefficients (a , b) for the kinetic models

Coefficient	Bioleaching	Acid leaching
a	0.0245 ± 0.0127	0.0398 ± 0.0260
b	1.0083 ± 0.1514	0.8486 ± 0.2011

Figure 4 shows uranium recovery (%) as a function of leaching time (days). The uranium extraction under acid leaching conditions reached a maximum value of $64 \pm 13\%$ w/w after 31 days. In the same figure (Fig. 4) is shown the kinetic model for uranium bioleaching. The biological leaching of uranium reached a maximum of $75 \pm 15\%$ w/w recovery after 55 days.

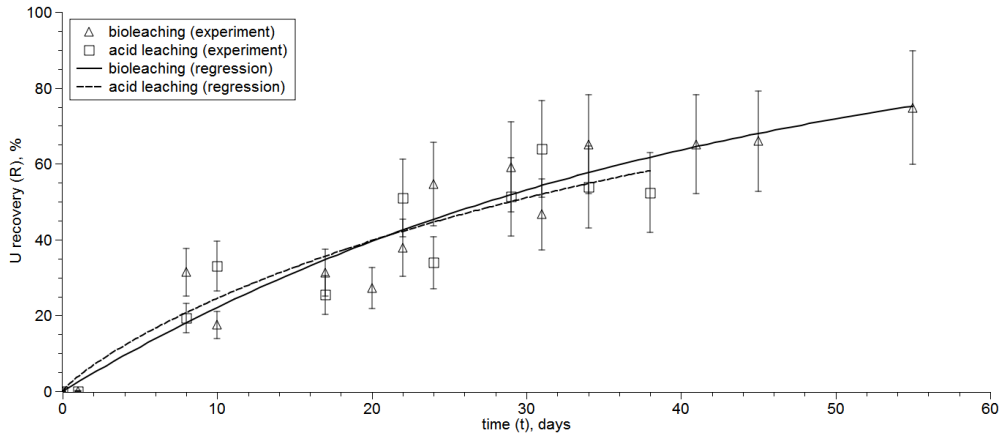


Fig. 4. Uranium extraction (%) as a function of leaching time (days)

The uranium leaching from the Radoniow ore is a typical liquid-solid leaching process, which can be described by the shrinking-core model (SCM), when the ore particle is regarded as spherical. SCM is the most popular model in hydrometallurgy (Tian et al., 2010; Levenspiel, 1999; Othusitse and Muzenda, 2015). References (Habashi, 1999; Levenspiel, 1999; Othusitse and Muzenda, 2015) stated that for the chemically controlled reaction at the interface (phase boundary controlled reaction) Eq. (5) the following equation can be used

$$k \cdot t = 1 - (1 - x)^{1/3} \quad (5)$$

where k is the apparent rate constant (day^{-1}), t is the leaching time (days), and x is the fractional conversion given by $x = C/C_o$, C is the concentration of uranium in the post-leaching solution ($\text{g} \cdot \text{dm}^{-3}$), C_o is the concentration of uranium in the raw material before experiments ($\text{g} \cdot \text{dm}^{-3}$).

By applying the equations to the experimental data and plotting the fractional conversion in relation to time, the relationship between the data and the reaction rate equations becomes apparent. The model obtained from Eq. (5) is illustrated in Figure 5 using the same experimental data as in Figure 4. If the plot of $1 - (1 - x)^{1/3}$ vs. t is linear then the shrinking-core model will be verified. This relationship is linear (Fig. 5). Therefore, the shrinking-core model is verified. The uncertainty of model $1 - (1 - x)^{1/3}$ (Fig. 5) was calculated using the exact differential method (Bures et al., 1967).

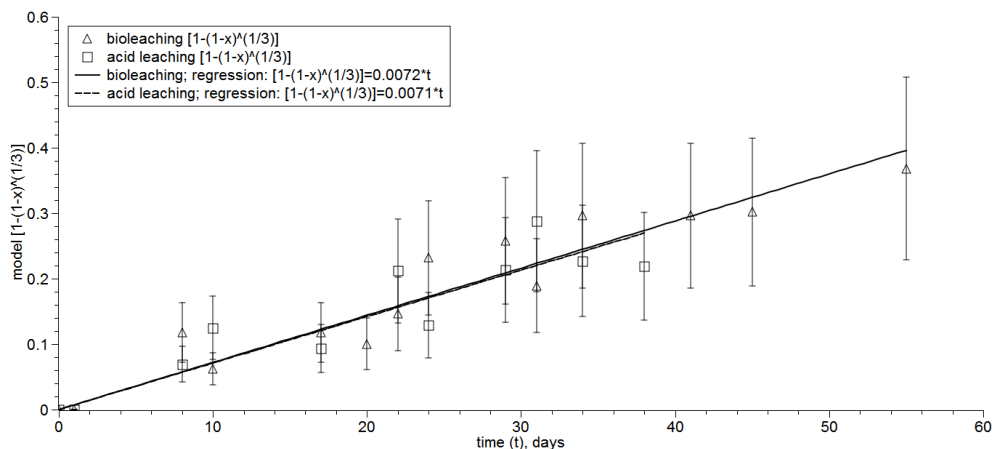


Fig. 5. Plot of the shrinking-core model showing the fractional conversion of uranium as a function of time

Effect of particle size

The particle size of the ore is significant in ore solubilization (Piestrzynski et al., 1996). Many authors show that the decrease in particle size enhanced metals extraction (Gajda et al., 2015).

The influence of particle size of ore in uranium sandstones from Krynica Morska, Poland with uranium content 355 ppm on the efficiency of uranium leaching was tested using 10 % $\text{H}_2\text{SO}_4/\text{MnO}_2$ system at 60 °C with a liquid/solid ratio 8:1 (vol./wt. basis) by (Gajda et al., 2015). Three fractions with different granulations were tested: <0.2 mm, 0.2–0.4 mm and 0.4–0.63 mm. Obvious influence of particle size on the metal recovery was not observed (Gajda et al., 2015). Slight influence of particle size on the metal recovery could be due to the mineralogical and elemental distribution within the sizes and interaction of the minerals and phases within the ore (Ghorbani et al., 2011). As reported (Tian et al., 2010), the permeability is related to ore granule size and the packed porosity. The smaller the ore granule size, the less permeability due to fluid channels becoming more flexuous and narrower with the smaller particle size of the ore.

Slight permeability of the ore layer appeared during the process (mass 150 g) at the top of the column under bioleaching conditions. Based on these observations, the changes in structural permeability of the ore were observed in both the biological and acid leaching columns. The mass fraction of 0.5–2.5 mm increased in the acid leaching column. However, mass of the same fraction decreased in the bioleaching column. Consequently, it is necessary to use ore with a high porosity, especially for biological processes. The decisive role played by the microorganisms (particularly the *Thiobacillus ferrooxidans* species) in uranium dissolution and ore disintegration was showed by (Munoz et al., 1995). In heap leaching case, particle size is large and liquid-solid contact is not perfect in contrast to a stirred tank experiment (Munoz et al.,

1995) even heaps are usually built using piping inside to provide good oxygen and carbon dioxide transfer. Besides, temperatures can vary considerably between different zones of the heap.

Conclusions

The experimental results prove that the effectiveness of the applied leaching processes for uranium recovery are different. The dissolution of uranium in the column under acid leaching conditions reached a maximum value of $64 \pm 13\%$ w/w after 31 days. The bioleaching of uranium reached a maximum of $75 \pm 15\%$ w/w after 55 days.

The changes in structural permeability of the ore in both columns were observed. In the bioleaching process is necessary to use ore with a high porosity. The experimental results showed that both leaching methods can be important and prospective methods for recovery of uranium from low-grade ore and wastes, such as industry tailings.

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