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Uranium in Poland: Resources and Recovery from Low-Grade Ores

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Abstract

The presented studies deal with an assessment of the possibility of uranium recovery from the low-grade uranium resources in Poland. Uranium was leached from the ground uranium ores with efficiencies in 81–100% range that depend on the type of ore and leaching solution used. In the next step, the post-leaching solution was treated by the solvent extraction or ion exchange chromatography to separate uranium from other metals present in the ore. The novel routes of leaching by using membrane methods were examined. The final product, “yellow cake,” was obtained in precipitation step. The studies of precipitation of uranium as ammonium diuranate or uranium peroxide from diluted uranium solutions are presented in this chapter. The work was completed with tentative economic analysis and environmental impact assessment along with radiation protection issues connected to uranium production.

Keywords: uranium ores, leaching, extraction, ion exchange chromatography, precipitation

1. Introduction

Continued interest in nuclear power and uranium industry revival is leading to the inevitable growing uranium demand. New sources of primary uranium will be derived from exploration and exploitation of lower grade ore bodies and also secondary resources as potential raw materials. In Poland, there are only low-grade uranium ores. The knowledge about a composition of a bedrock, uranium speciation and its composition with rock constituents is important for the design of the effective technology of extraction of uranium from low-grade

ores. The significant resources of uranium are also in unconventional raw materials, e.g. phosphates, nonferrous metal ores, carbonates, monazite sands, black shales, hard coal and brown coal, as well as sea water, from which it can be obtained as a minor by-product. In Polish ores, uranium usually is accompanied by other valuable metals, e.g. V, Mo and lanthanides that can be obtained simultaneously in the technological process to improve the economics of elaborated technology.

2. Uranium resources in Poland

Prospection of uranium deposits in Poland started in the late 1940s of the last century. In the years 1948–1963, Sudetes were the main region of exploration and exploitation of uranium resources [1]. Although more than 100 occurrences of uranium mineralization have been found in the Sudetes, only a few were exploited because of sufficient content of this metal. Uranium was also found and exploited as a by-product from iron sulfide deposit in Rudki (“Staszic” mine) in the Holy Cross Mountains. In this time, approximately 650–700 Mg of uranium was extracted from Polish ores and exported to Soviet Union [1, 2] (Table 1).

Polish uranium vein-type deposits in the Sudetes are related to metamorphic rocks. Moreover, uranium mineralization occurs in the sedimentary formation of Inter-Sudetic Depression:

Name of mine	Resources [Mg]	Exploited [Mg]	Main U minerals	Deposit type	U content [%wt]
Radoniów	375	214	Uraninite, pitchblende, metauranocircite, autunite, torbernite, uranopilite	Vein	0.17
Podgórze	280	199	Pitchblende, uranophane, autunite	Vein	0.2
Rubezal	0.5	0.5	Pitchblende	Vein	0.24
Wolność	118	94	Pitchblende, secondary minerals	Vein	0.1–0.2
Miedzianka	14.7	14.7	Pitchblende, secondary minerals	Vein	0.61
Mniszków	4.5	4.5	Pitchblende, secondary minerals	Vein	0.42
Wiktoria	0.28	0.28	Pitchblende, secondary minerals	Vein	n.d.
Wołowa Góra	2.5	2.5	Brannerite, secondary minerals	Vein	n.d.
Wojcieszyce	14.4	12.3	Pitchblende, asselbornite, autunite	Vein	n.d.
Okrzeszyn	938	3	Pitchblende, organometallic compounds	U-rich hard coal	0.05–0.11
Grzmiąca	792	3	Pitchblende, secondary minerals	Sandstone	0.054
Wambierzyce	217.5	0	Organometallic compounds	Black shale	0.01–0.03
Kletno-Kopaliny	20.71	20.7	Pitchblende, Torbernite	Vein	0.26–1

n.d. - no data.

Table 1. Uranium exploitation of Sudetes deposits [1–4].

Grzmiąca deposit related to Upper Carboniferous Sandstones, Okrzeszyn deposit related to uranium-rich Upper Carboniferous hard coal seams and Wambierzyce related to Lower Permian Walchia Shales.

In 1956, Polish Geological Institute (PGI) has initiated a new phase of prospecting of uranium. Additionally, parallel studies, based on all available geological and geophysical borehole data from the whole area of Poland, were conducted. The studies have led to the description of uranium mineralization in the Oligocene Menillite Shales of the Carpathians, the Carboniferous of the Upper Silesian Coal Basin and Zechstein copper-bearing shale [3]. Nevertheless, these uranium occurrences have no economic importance due to very low content of uranium, very small resources and close relationship with clay minerals and organic matter.

During prospection conducted by PGI, uranium mineralization in the Ordovician dictyonema Shales (Podlasie Depression) and the more perspective Lower and Middle Triassic sediments in the Peribaltic Syncline (Vistula Spit area) were discovered and explored (**Table 2**).

Uranium mineralization of Ordovician dictyonema Shales was found in rock layers of thickness from several centimeters up to 4 m (average thickness is about 2.7 m). In vertical profile black shale series was found passing upward brown shales, replaced above by the light beige shales and phosphates. Uranium occurs mainly in black shales. Apart from uranium, higher concentration of other trace metals was observed. For black shales, concentration (geometric mean) of chosen metals was: U 38 [mg/kg]; Th 16 [mg/kg], Cu 236 [mg/kg], La 43 [mg/kg] and V 1508 [mg/kg]. For brown shales, concentration geometric mean was three times lower for most metals, and it was U 38 [mg/kg], Th 18 [mg/kg], Cu 169 [mg/kg], La 45 [mg/kg] and V 678 [mg/kg]. In the black dictyonema shales, uranium showed the strongest correlation with molybdenum (0.83), lead (0.57) antimony (0.52), cadmium (0.50), silver (0.36), lithium (0.28) and beryllium, while in brown dictyonema shales with vanadium (0.69), selenium (0.87), molybdenum (0.78), antimony (0.89), copper (0.34), cobalt (0.66), nickel (0.75) and REE (0.41) [7].

The highest uranium-rich Triassic rocks have been found in the middle part of Peribaltic Syncline, in the rocks of Upper Bunter. The richest uranium mineralization is related to fine-grained, grey and green-grey sandstones, which occurs on the Vistula Spit area. It was found that uranium concentration in the sandstones is very variable and ranges from 4.2 mg/kg even up to 1.5%_{wt}. Higher concentration of some trace metals were also found in these rocks

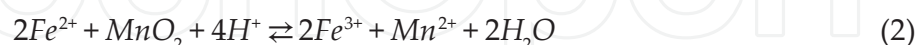
	Ordovician dictyonema Shales	Triassic Peribaltic sandstones
Deposit type	Rock types with elevated uranium contents (black shales)	Sandstones
Speculative resources [Mg]	88,850	20,000
Depth of U retention [m]	400–1200	750–1170
Uranium minerals	Organometallic compounds	Coffinite, pitchblende, (inclusion in pyrite, galena and clausthalite)

Table 2. Ordovician dictyonema Shales and Triassic Peribaltic sandstones characteristics [5, 6].

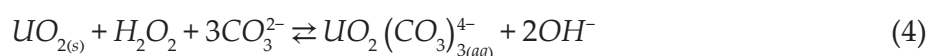
(geometric mean): Th 6 [mg/kg], Cu 24 [mg/kg], La 31 [mg/kg] and V 195 [mg/kg]. Uranium related to Triassic sandstones showed the strongest correlation with lead (0.92), yttrium (0.92), silver (0.76), copper (0.75), antimony (0.7) and cobalt (0.44) [8].

3. Uranium extraction from low-grade and secondary resources: From ore to yellow cake

Uranium, more common element in the Earth's crust occurring in rocks, soil, rivers and ocean waters, has to be extracted from the raw material in a complex hydrometallurgical process [2]. The effect of ore mineralogy and mineral liberation of solid materials on the leaching behavior of uranium is not well defined. Uranium usually is accompanied by other valuable metals, e.g. V, Mo, Ag, Co and lanthanides that can be recovered in the technological process to improve the economics of the whole venture [9]. The procedure of uranium extraction must be designed to fit specific characteristics of the source material; however, the general procedure is similar for most of the ores and involves many separation steps. The basic stages are crushing and grinding, leaching, solid-liquid separation, ion exchange or solvent extraction and finally precipitation of the product, yellow cake – U_3O_8 (**Figure 1**) [10, 11]. In the beginning, the mined ores must be crushed and ground to make the uranium ores more susceptible to uranium extraction by leaching. The optimal particle size in leaching process is 0–0.2 mm. So small particles can be readily suspended to expose the uranium minerals on the action of lixiviant. Such a pre-prepared material could be leached with acidic (sulfuric acid, hydrochloric acid, etc.) or alkaline (carbonate) solutions [6, 12]. Tetravalent uranium has low solubility in both types of solutions. For this reason, the first step in uranium leaching process is oxidation of uranium(IV) to uranium(VI) form. The use of oxidants, e.g. manganese oxide, potassium permanganate, sodium chlorate or hydrogen peroxide, increases the leaching ability of uranium in water. In acidic leaching, uranium oxidation requires the presence of ferric ion, regardless of used oxidizing agents [10]. The oxidizing agent oxidizes ferrous ion to ferric ion that is oxidant for the uranium as shown in Eqs. 1, 2 and 3.



In alkaline leaching, the oxidizing agent oxidizes directly uranium as shown in Eq. 4.



If uranium is closely associated with the organic compounds, the efficiency of leaching is low. The ores that contain the organic matter, e.g. dictyonema shales, have to be pre-treated by calcination. The samples of sandstones that contained less organic matter (below 0.1%) are

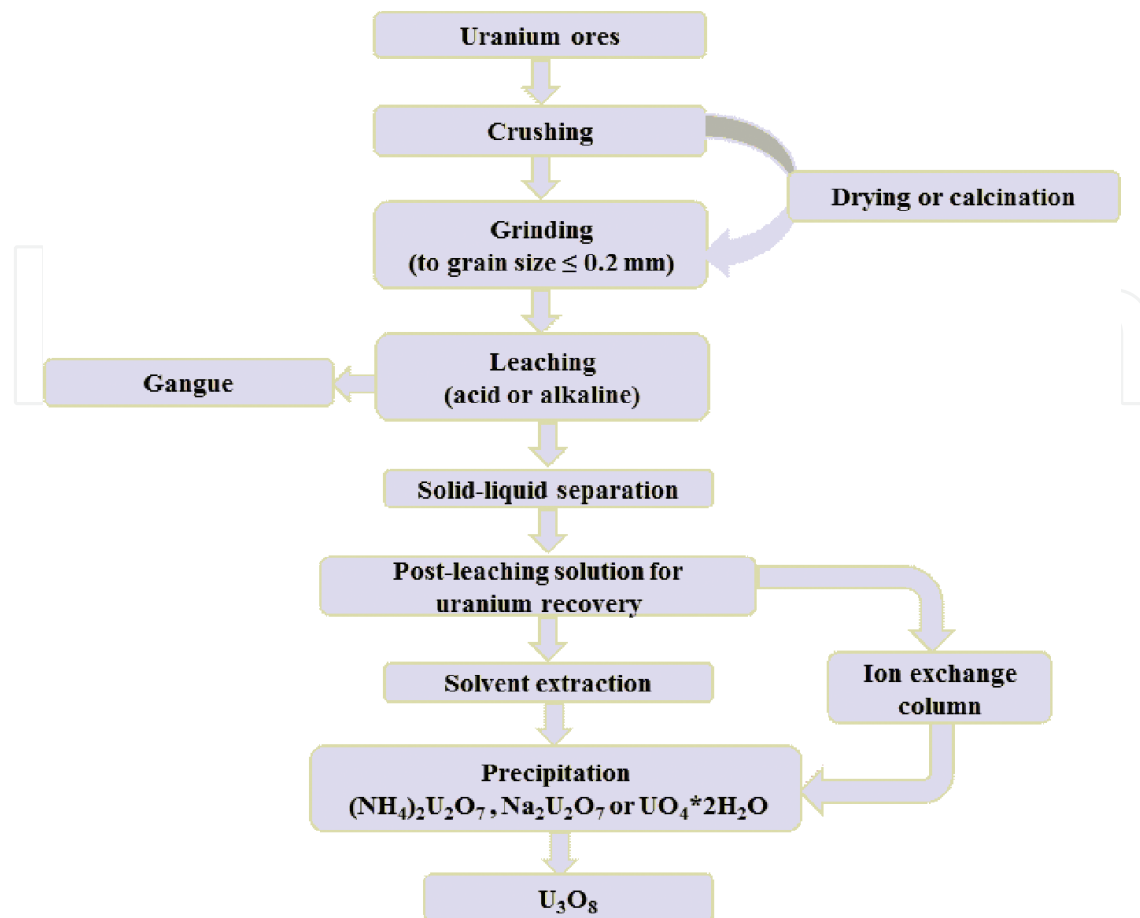


Figure 1. Treatment of uranium ores.

not calcinated in the oven. The post-leaching solution is separated from the ores residue by filtration. The concentration of uranium and other elements in post-leaching solution may be determined using ICP-MS analyses [13]. The leaching efficiency is defined as the ratio of the amount of the metal in post-leaching solution to the amount of the metal in the ore sample according to the formula (Eq.5):

$$E = \left(\frac{m}{m_0} \right) \cdot 100\% \quad (5)$$

where m is the total mass of the metal recovered in post-leaching solution and m_0 is the total mass of the metal in the ore sample.

Many factors influence the leaching process among others, the kind and concentration of leaching medium, size of ore particles, liquid to solid ratio, temperature, pressure and the type of oxidizing agent.

The predominant process for recovery of uranium from rocks is the leaching with sulfuric acid [14–16]. The efficiencies of leaching in sulfuric acid environment reach 85–95%. However, this method is not appropriate for the leaching of uranium from carbonate rocks due to high acid consumption [17, 18]. It is worth to note that the alkaline leaching is more selective for uranium in comparison with acid processing. Uranium was selectively leached by the mixture of

sodium carbonate, sodium hydroxide and hydrogen peroxide from hydrous oxide Egyptian monazite [19] and from Polish ores [6, 12]. The leaching test using deionized water as a leaching solution (pH = 5.7) was also performed on Jordania carbonate rocks [20]. The leaching efficiency was 9% using deionized water as a leaching solution.

3.1. The leaching of Polish domestic ores

In Poland, as it was said earlier, there are occurred mainly two types of uranium ores: dictyonema shales and sandstones. The content of metals in post-leaching solution is very depending on the initial composition of the ore and the used procedure of extraction. The effect of ore mineralogy and mineral liberation on the leaching behavior of uranium and other metals is not well defined. For this reason, the prediction of results of the treatment of ores is not possible and it was necessary to make an experimental work. It showed that sandstones were more readily leachable in comparison with the dictyonema shales. In the leaching by acid, all metals accompanying uranium in the ores were also present in acid post-leaching solutions [6]. The best results of acid leaching of dictyonema shales were obtained in the leaching with 10% H_2SO_4 during 8 hours at 80°C. The efficiencies of uranium leaching from different ore materials were in the range of 64–81%. Other metals were leached with the following efficiencies: Th 67–80%, V 25–52%, Mo 33–78%, Cu 28–52% and La 31–66%. The leaching of sandstones with 10% sulfuric acid was carried out at 60°C. Uranium was leached with efficiency 71–100%; efficiencies of leaching other metals were: Th: 13–62%, Cu: 10–67%, Co: 8–57%, La: 24–60%, V: 28–58%, Yb: 26–67% and Fe: 11–47%.

In the case of alkaline leaching, only three or two metallic components of the ores were detected in post-leaching solution: U, Mo and V (dictyonema shales) or U and small amounts of V (sandstones). U from calcinated samples of dictyonema shales was extracted with 42% efficiency, molybdenum with 24% and vanadium with ca. 8% efficiency. In the case of sandstones, 57–92% of uranium and 2–22% of vanadium were leached with a mixture of sodium carbonate and bicarbonate. The comparison of uranium leaching efficiencies depending on lixiviant and leaching method is presented in **Figures 2 and 3**.

3.2. Recovery of uranium from the post-leaching solution

The above-described process, the solid–liquid extraction, is a very important stage in the technology of uranium production from the uranium ores. The separation of solid residue from liquid leaves the post-leaching solution that is a mixture of different metal ions. Uranium and other metals can be recovered from post-leaching solutions by solvent extraction [21–24] followed by stripping to aqueous phase [25, 26] or by ion exchange [27, 28].

3.2.1. Recovery of uranium by solvent-solvent extraction

Solvent extraction is a comprehensive technique for separation of ionic solutes. The uranyl ion (UO_2^{2+}) forms complexes with various extracting agents, among them tributylphosphate (TBP), di(2-ethylhexyl)phosphoric acid (DEHPA), triethylamine (TEA), tri-*n*-octylamine (TnOA), trioctylphosphine oxide (TOPO) and calixarenes, e.g. hexasodium 37,38,39,40,41,42-hexa(carboxymethoxy)calix[6]arene-7-5,11,17,23,29,35-hexasulfonate (**Figure 4**, calix[6]arene: $\text{R}^1 = \text{SO}_3\text{Na}$,

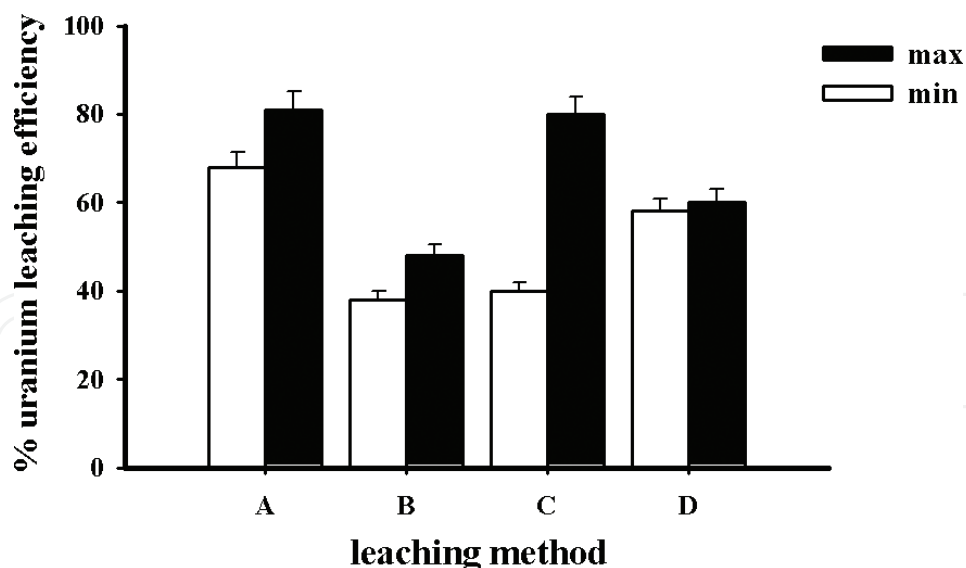


Figure 2. Efficiency of leaching uranium from dictyonema Shales using different methods. (A) Calcinated sample, lixiviant: 10% H_2SO_4 , liquid/solid ratio of 8:1 (vol./wt. basis), oxidizing agent: MnO_2 , 80°C, 8 h. (B) Calcinated sample, lixiviant: 5% Na_2CO_3 /5% NaHCO_3 , liquid/solid ratio of 8:1 (vol./wt. basis), oxidizing agent: MnO_2 , 80°C, 8 h. (C) “acid-cure”: 2 g of ground uranium ores were treated with 95% H_2SO_4 for 18 days, 25°C, 8 h. (D) Sintered sample with addition of 10% NaCl at 840°C during 3 h than leaching with 5% H_2SO_4 , MnO_2 , 80°C, 8 h.

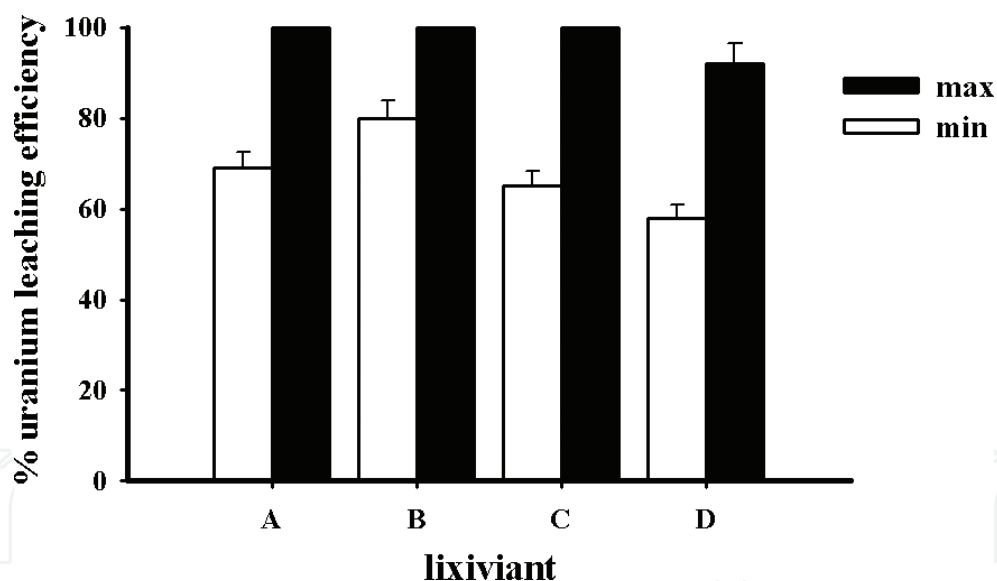


Figure 3. Efficiency of leaching uranium from sandstones by various lixiviants, liquid/solid ratio of 8:1 (vol./wt. basis). (A) 10% H_2SO_4 , oxidizing agent: MnO_2 , 60°C, 1 h. (B) 10% HCl, oxidizing agent: 30% H_2O_2 , 60°C, 1 h. (C). 8% NaOH/18% Na_2CO_3 , oxidizing agent: 30% H_2O_2 , 60°C, 1 h. (D) 5% Na_2CO_3 /5% NaHCO_3 , oxidizing agent: KMnO_4 , 60°C, 1 h.

$\text{R}^2 = \text{CH}_2\text{COOH}$). Calixarenes are a well-known family of macrocyclic molecules with broad field of potential applications in chemical, analytical and engineering materials area [29]. The reason of growing interest in these macrocycles is not only their easy synthesis through well-established and simple methods but also the possibility of shaping through functionalization with the appropriate groups R^1 and R^2 . The calixarenes are applied for UO_2^{2+} complexation with high efficient results in terms of stability and selectivity [30].

TBP, neutral organophosphorus extractant, is probably the most known chelating agent. It was used on the commercial scale for the recovery of uranium (VI) not only from its ores but also from the spent nuclear fuel [31]. The selectivity of TBP is not high, similarly as its radiolytic stability. For this reason, other organophosphorus extractants, among them DEHPA, are applied in the technology of uranium production. DEHPA saponifies in stripping phase and wherefore the third phase is formed between the organic solvent and the aqueous phase. It can be prevented with a modifying agent, a suitable non-ionic surface active substance. The modifying agent like long-chain alcohols, alkyl phosphonates, alkyl phosphates and alkyl phosphine oxides have also a beneficial synergistic effect on the distribution ratio of uranium. One of such agents is TBP. The very good results were obtained in the extraction of uranium from the solutions resulting from leaching Polish uranium ores by using the mixture of DEHPA and TBP (0.2 M: 0.2 M) [32]. Before the solvent extraction, the post-leaching solutions were acidified to pH 1. This especially applied to the liquors from carbonate leaching. However, sometimes it was also necessary to adjust appropriate pH of the solution from acidic leaching. During the extraction process, uranium passes from the aqueous solution to the organic solution by using an extracting agent. The metal ions that have been extracted by the organic phase should be stripped by an aqueous phase in the stripping (re-extraction) process. A number of reagents are known in the literature to strip uranium from loaded extracting agents such as carbonates, acids, nitrates, chlorides, sulfates and hydroxides. In this study, the best results were obtained when stripping experiments were carried out with sodium carbonate or ammonium carbonate solutions. The extraction efficiency (%E) was calculated by the Formula (6):

$$\%E = \frac{100 \% \cdot D_c \cdot V_{aq}}{D_c + V_{org}} \quad (6)$$

where D_c is the distribution ratio, defined as the ratio of concentration of metal in organic phase over its concentration in aqueous phase, V_{aq} is the aqueous phase volume, and V_{org} is the organic phase volume [33].

The stripping percentage, %S was determined by the relationship (7):

$$\%S = \frac{100 \% \cdot D_s \cdot V_{aq}}{D_s + V_{org}} \quad (7)$$

where D_s is the distribution ratio of metal in stripping phase over its concentration in organic phase [33].

%R percent of the recovery of uranium in extraction/stripping process was determined by the relationship (8):

$$\%R = \frac{\text{metal in the stripping phase}}{\text{metal in post-leaching liquor}} \cdot 100\% \quad (8)$$

The obtained results were satisfying; the overall recovery (%R), extraction efficiency (%E) and stripping (%S) reached even 98%. Apart from uranium, the other elements were also analyzed. The results of extraction/stripping processes of alkaline and acidic post-leaching solutions are reported in **Tables 3** and **4**, respectively. The purification of uranium from accompanying metals from acid leaching solution was only in part. The efficiency of recovery of uranium

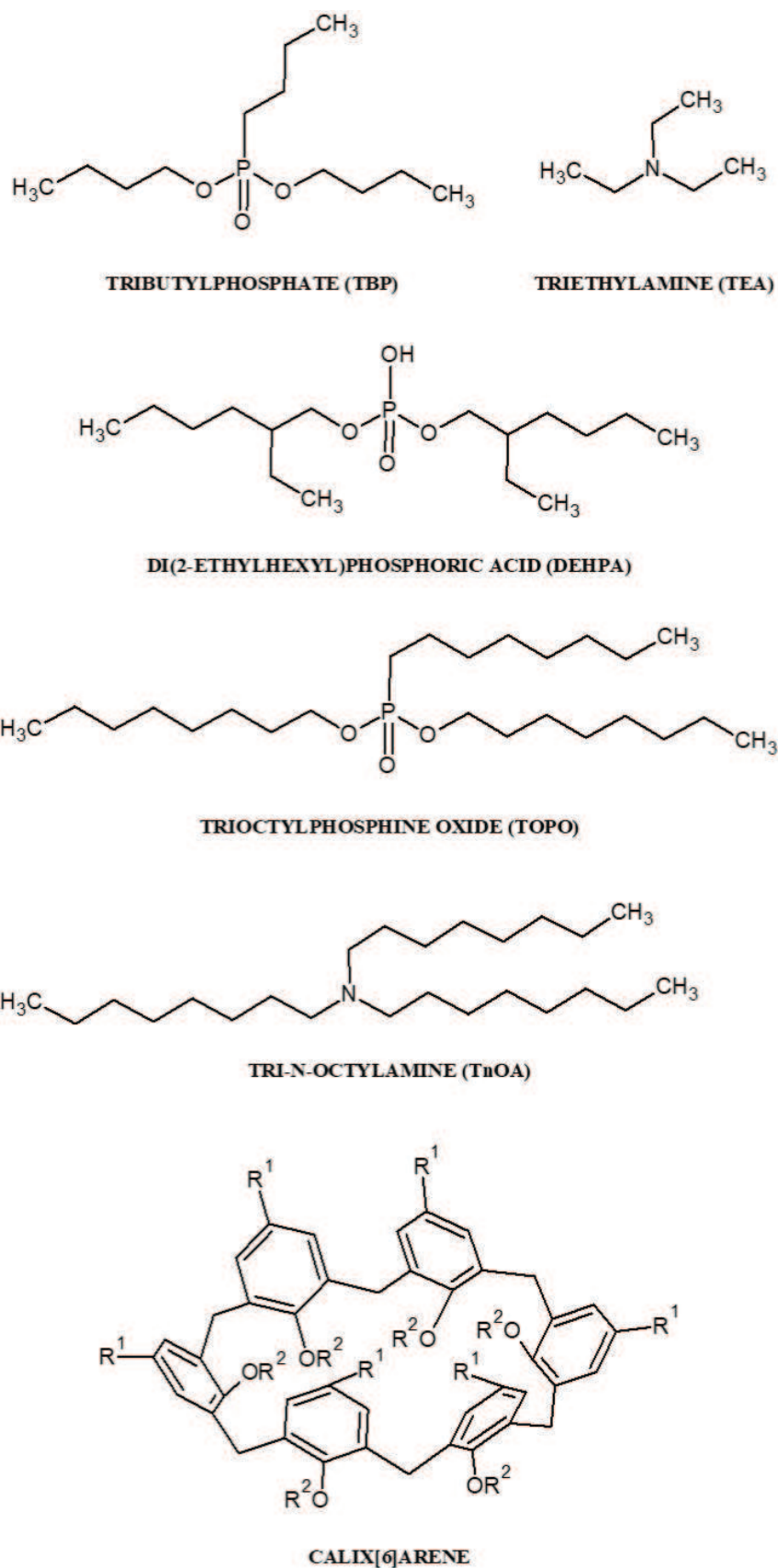


Figure 4. The extracting agents using for the separation of uranium from the solution.

Post-leaching solution		Extracting phase		Stripping phase 0.5 M (NH ₄) ₂ CO ₃			Stripping phase 0.5 M Na ₂ CO ₃		
Metal	C _a [ppm] ^a	C _b [ppm] ^b	%E	C _c [ppm] ^c	%S	%R	C _d [ppm] ^c	%S	%R
U	25 ± 1.25	25 ± 1.25	100	24.7 ± 1.2	99	99	24.7 ± 1.2	99	99
Th	<0.1	—	—	—	—	—	—	—	—
Cu	14 ± 1.4	0	0	—	—	—	—	—	—
Co	0.5 ± 0.05	0	0	—	—	—	—	—	—
Mn	27 ± 2.7	0	0	—	—	—	—	—	—
La	0.2 ± 0.02	<0.001	<0.5	—	—	—	—	—	—
V	3 ± 0.3	0.75 ± 0.08	25	0.23 ± 0.02	31	8	0.23 ± 0.02	31	8
Mo	0.8 ± 0.08	0	0	—	—	—	—	—	—
Yb	0.2 ± 0.03	0.2 ± 0.03	100	0.19 ± 0.03	99	99	0.17 ± 0.03	85	85
Fe	230 ± 23	74 ± 7.4	32	21 ± 2.1	28	9	24 ± 2.4	32	10

^a C_a—concentrations of metals in post leaching solution,
^b C_b—concentrations of metals in organic phase from extraction process,
^c C_c, C_d—concentrations of metals in stripping phase.

Table 3. Extraction and stripping efficiencies of metals from acidic post-leaching solution, [DEHP]:[TBP] 0.2 M:0.2 M, temperature: 22°C, pH 1, phase ratio (*organic/aqueous*) 1:1.

was high, but the final solution was contaminated by iron and small amounts of other metals: vanadium and ytterbium. On the other hand, the purification of uranium from alkaline post-leaching solution was almost complete (**Table 4**). The extraction, followed by stripping step gave pure uranium solution. It is worthy to mention that the single, one-stage extraction of uranium from acidic post-leaching liquors is not sufficient to separate pure uranium. Further purification and separation of uranium from accompanying metals could be performed by ion exchange chromatography or a sequence of ion exchange/extraction treatments.

3.2.2. Recovery of uranium by ion exchange

The ion exchange is a very efficient method that can be used for separation of uranium from other metals. The separation of uranium from acid pregnant leach solution obtained from Polish uranium ores, using commercially available, strongly basic anion exchanger, Dowex 1 was investigated [28]. The feed solution was introduced into the column. The complexes of uranium, vanadium and molybdenum were adsorbed on Dowex 1 and then they were eluted with 0.15 M H₂SO₄, followed by 1 M sulfuric acid. The first eluent removed the vanadium complex from the column. The second eluent allowed to obtain fraction of uranium complexes. The molybdenum complexes are very strongly fixed in anion exchange resin. They can be eluted only in part by 1 M H₂SO₄. Wherefore the uranium fraction can be contaminated with molybdenum. It is worth to note that the purification of the acid pregnant solution from leaching of sandstones that does not contain the molybdenum gave a pure uranium fraction. In this work, there was also considered the recovery of other valuable metals present in uranium

Post-leaching solution		Extracting phase		Stripping phase 0.5 M (NH ₄) ₂ CO ₃			Stripping phase 0.5 M Na ₂ CO ₃		
Metal	C _a [ppm] ^a	C _b [ppm] ^b	%E	C _c [ppm] ^c	%S	%R	C _d [ppm] ^c	%S	%R
U	20 ± 1	20 ± 1	100	19.8 ± 1	99	99	19.8 ± 1	99	99
V	0.63 ± 0.06	<0.01	—	—	—	—	—	—	—
Mo	0.72 ± 0.07	0	0	—	—	—	—	—	—

^aC_a—concentrations of metals in post leaching solution,
^bC_b—concentrations of metals in organic phase from extraction process,
^cC_c, C_d—concentrations of metals in stripping phase.

Table 4. Extraction and stripping efficiencies of metals from alkaline post-leaching solution, [DEHP]:[TBP] 0.2 M:0.2 M, temperature: 22°C, pH 1, phase ratio (*organic/aqueous*) 1:1.

ores, especially the lanthanides. They can be separated from the effluent from anion exchange column by using the second column filled with strongly acidic cation exchanger (DOWEX50 WX8) (**Figure 5**) [5]. The efficiencies of recovery of metals were almost quantitative: 93% for uranium and 99% for lanthanides were recovered. The other metals accompanying uranium in their ores were not separated and were present in the effluent from columns.

3.3. Precipitation of uranium yellow cake

The solvent extraction and ion exchange processes were a part of the research on the possibility of uranium extraction from domestic resources in Poland. The next step was the precipitation of precursors of yellow cake - U₃O₈. From acidic solutions, uranium is precipitated in the form of ammonium or sodium diuranate, uranium peroxide and uranium trioxide by the addition of neutralizers such as sodium hydroxide, magnesium oxide or aqueous ammonia (**Figure 6**) [34, 35]. In all cases, the final product is yellow uranium salt, commonly known as yellow cake.

The studies of precipitation of uranium as two different salts: (NH₄)₂U₂O₇ and UO₄·2H₂O from the model uranium solution (UO₂(NO₃)₂ in 2 M H₂SO₄) were performed (respectively, Eqs. 9 and 10). As was proved, the influence of temperature and concentration of uranyl ions in the solution was significant. The precipitation of ammonium diuranate was carried out in the temperature range of 40–90°C, at pH 9–11. The concentration of uranium was between 0.3 and 0.7 mg/L. The obtained yield was really high 83–98% [36]. It is significant that this salt was precipitated from solutions containing a low concentration of uranium (0.3–0.5 mg/mL). The precipitation step was followed by calcination step at temperature 750°C, in which U₃O₈ was formed.



This procedure was used for obtaining “yellow cake” from the effluent from anion exchanger, Dowex 1, that was described above. The yield was ca. 92% [28].

Uranium peroxide hydrates can be synthesized by dropping hydrogen peroxide to the acidic solution of uranyl ions, as it is shown in Eq. 8. Uranium peroxide can be precipitated from

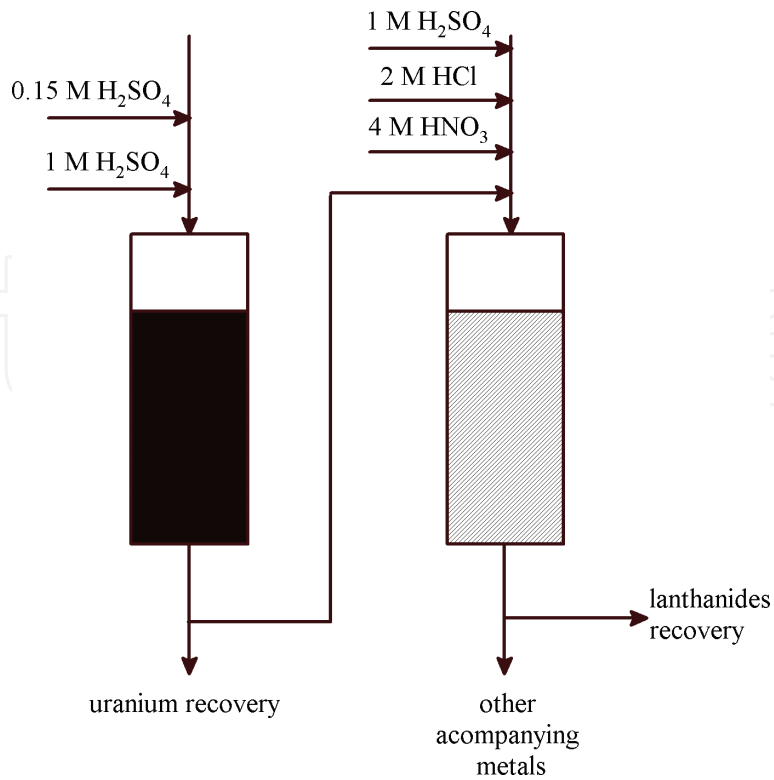


Figure 5. Set of two columns with strongly basic anion exchanger (DOWEX1 X8) and strongly acidic cation exchanger (DOWEX50 WX8).

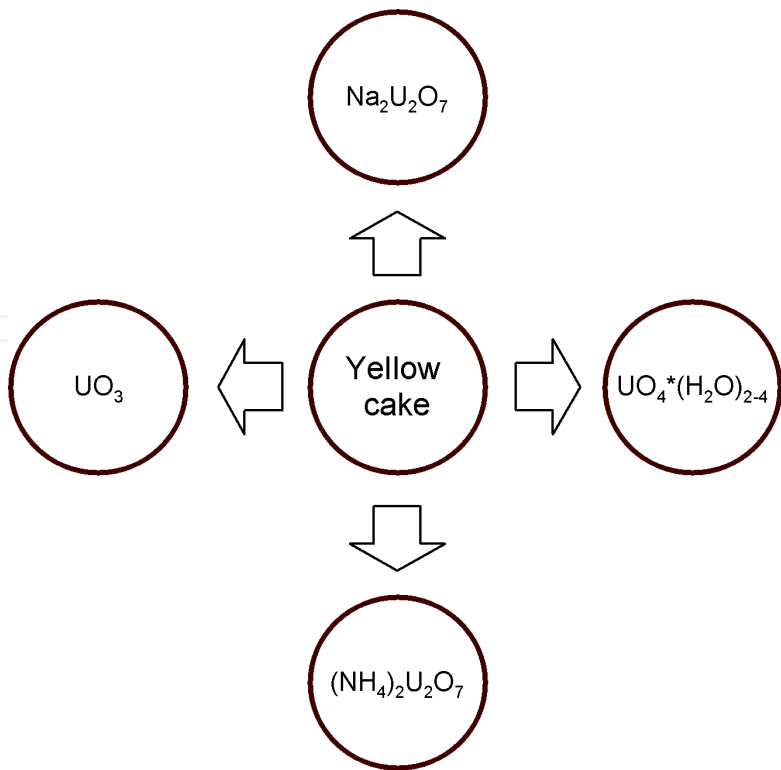


Figure 6. Precipitation of precursors of yellow cake.

eluted solution with concentration of uranium 0.5–0.9 g/L with high yield, almost quantitatively. It was found that optimal pH of the solution was between 9 and 11. The yield of the process provided at temperature 60°C was rather low, 17% for the solution with 0.5 g/L of uranium and 63% for the solution with 0.9 g/L of uranium. Increasing the temperature up to 90°C definitely improved efficiency, 93 and 99%, respectively.



4. Novel methods of uranium extraction by using membrane methods

Membrane processes and effective separation techniques can be applied in uranium technology. The first of proposed applications of membrane techniques was leaching of uranium from the ores with separation of solid and liquid phases in a helical membrane contactor equipped with rotor. [37]. The second one was recovering of uranium from post-leaching solutions by using solvent extraction with application of the membrane contactors with polypropylene porous membranes [38].

4.1. Leaching of uranium using membrane contactor

As an alternative method of uranium leaching from the ores, the membrane contactor was proposed. The main advantage of using the membrane contactor is a possibility of combining two processes: leaching and separation of the solid phase from post-leaching solutions in one apparatus. Such an approach results in the reduction of total cost of operation with no consequences to the separation efficiency. Another advantage of using the membrane contactor is the possibility of conducting the leaching process at room temperature, which results in less energy consumption.

In the experiments, the membrane module with helical flow generated by rotating part, equipped with a tubular metallic membrane with the pore size of 0.1 μm, was applied. The scheme of the experimental set-up is presented in **Figure 7**. The sample of uranium ore with manganese dioxide, and a solution of 5% sulfuric acid, was placed in the stirred feed tank. Then, the suspension of uranium ore (feed) was transferred with a gear pump to the membrane contactor where the process of leaching was proceeded. The leaching process was conducted in a closed system, which means that permeate and retentate streams were recycled to the feed tank. The process parameters were as follows: velocity of the feed flow (Q_s) was changed in the range of 1.1×10^{-5} – 2.2×10^{-5} m³/s and rotation frequency of the rotor (Ω) from 0 to 2500 rpm.

The results of uranium leaching conducted in the membrane contactor were compared with those obtained in experiments carried out using mixer-settler system. Leaching process using mixer-settler system was described in detail elsewhere [12]. The process was conducted in the stirred tank at 80°C for 8 h, using 10% sulfuric acid. The results of the experiments are collected in **Table 5**. As can be observed results of experiments conducted in the membrane contactor were comparable to those obtained by leaching process conducted in the mixer-settler

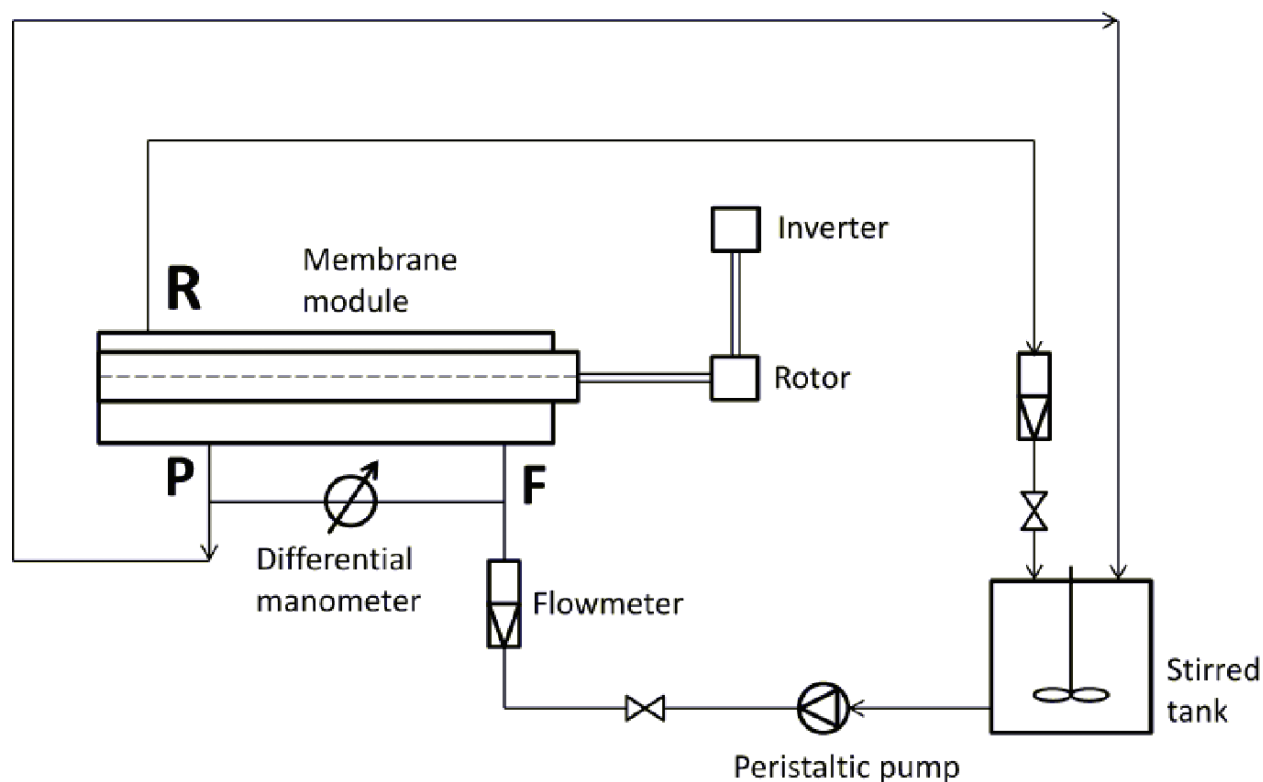


Figure 7. Experimental set-up for uranium leaching using membrane contactor.

system. The conducted experiments also have shown that both considered process parameters: velocity of the feed flow (Q_S) and a rotation frequency of the rotor (Ω) had an influence on the leaching efficiency of uranium and associated metals. When the velocity of the feed flow is considered, it can be noticed that an increase of this parameter results in an increase in the leaching efficiency of all analyzed metal ions. The increase in the rotation frequency of the rotor led to an increase in the leaching efficiency. However, this relation is clear only for the lower velocity of the feed flow ($Q_S = 1.1 \times 10^{-5} \text{ m}^3/\text{s}$). In case of higher feed velocity, a visible improvement in leaching efficiency with increasing the rotation frequency was not observed.

4.2. Extraction of uranium using membrane contactor

The new approach for the liquid–liquid extraction of uranium involves the membrane contactor which enables effective contact of two phases engaged in the process. The two phases are separated by the membrane and species are transferred from one phase to the other by the diffusion mechanism. During the extraction in the membrane contactor, ions are received by the organic phase from the feed (aqueous phase) until thermodynamic equilibrium is reached.

In the experiments, an installation for extraction of uranium equipped with the membrane Liqui-Cel® Extra-Flow contactor produced by CELGARD was used. The scheme of the installation is presented in **Figure 8**.

The module contains microporous hollow fiber membranes made of a polypropylene (PP). The experimental set-up consists also of thermostat, two micropumps, flow meter and temperature sensor. The first stage of the work was a selection of process conditions. Appropriate selection of

Leaching in the membrane contactor					
Process parameters		Leaching efficiency, %			
Q_{gr} [m ³ /s]	Ω , [rpm]	U	La	Th	V
1.1×10^{-5}	0	49.2	21.2	57.9	14.2
1.1×10^{-5}	1000	54.6	64.9	57.4	16.9
1.1×10^{-5}	1500	53.9	67.0	62.5	18.2
2.2×10^{-5}	0	67.5	75.9	75.9	21.8
2.2×10^{-5}	1000	68.9	77.9	64.6	25.6
2.2×10^{-5}	1500	56.7	65.5	65.5	18.0
2.2×10^{-5}	2000	45.7	61.0	59.7	16.7
2.2×10^{-5}	2500	63.9	94.1	25.8	25.1
Leaching in the mixer and settler system					
Process conditions			Uranium leaching efficiency, %		
80°C, 8 h			73.0		

Table 5. Leaching efficiency of uranium and accompanied metals obtained by two different methods of leaching.

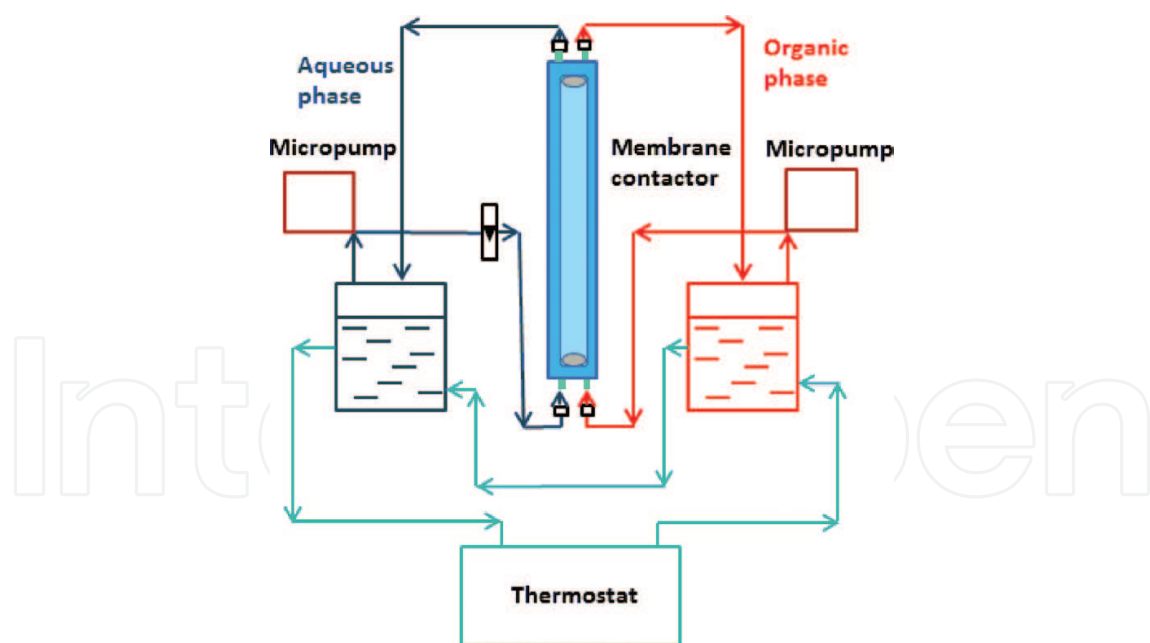


Figure 8. The scheme of the installation for extraction of uranium using membrane contactor.

hydrodynamic conditions in the membrane contactor eliminated the possibility of wetting the membrane and allowed stable working conditions of the apparatus. After a series of preliminary studies, it was found that a proper flow rate for the aqueous and organic phase (feed) is 98.11 and 5.95 L/h, accordingly. The flow of two phases in the system was arranged in co-current mode.

The next step of the work was a selection of extracting agents appropriate for the membrane process. Tributyl phosphate (TBP), triethylamine (TEA), di(2-ethylhexyl)phosphoric acid (DEHPA), tri-*n*-octylamine (TnOA) and trioctylphosphine oxide (TOPO) (see **Figure 4**) were considered as a potential extracting agents. The extraction efficiency (%E) was calculated by Eq. 6 (see above).

After preliminary experiments comprising determination of extraction efficiency, di(2-ethylhexyl)phosphoric acid (DEHPA) was found to be most favorable. The tests were performed using both model and real solutions. The results of experiments carried out using the model solution of uranyl nitrate in 5% H_2SO_4 are summarized in **Figure 9**. They show that the kinetics of membrane extraction is similar for different concentrations of uranium. However, the fastest extraction occurred for solutions with low concentrations of uranium. For concentration of 0.1 g/L, extraction efficiency reached a constant value after less than 1 h, while for concentration of 0.3 g/L equilibrium state was reached after about 2 h. It was also proved that an initial uranium concentration has great importance for extraction efficiency. The highest efficiency of the extraction process, reaching over 90%, was achieved in case of the solution with a concentration of 0.1 g/L, while the lowest with a concentration of 0.3 g/L.

The integrated process of extraction and stripping conducted in continuous mode was also investigated. This process includes two membrane modules, one for extraction and the other for back extraction. It was proved that in case of extraction/stripping process of real post-leaching solutions the high values of stripping and recovery of uranium were obtained. Using this process, it is possible to remove some metallic components from post-leaching liquors like Cu, Co and Ni. Such metals like Zn, Cr, Mo and Sb present in the ores were removed at the acid leaching stage.

Application of the membrane processes in the technology of the uranium recovery is very beneficial. The membrane contactors can be applied for recovery of uranium and associated metals from uranium ores as well as for the extraction of uranium from the post-leaching solutions.

Extraction with the use of membrane contactors has many advantages over conventional methods of the extraction of uranium, like no fluid/fluid dispersion, no emulsion formation, no flooding at high flow rates, low solvent holdup, known and constant interfacial area, easy

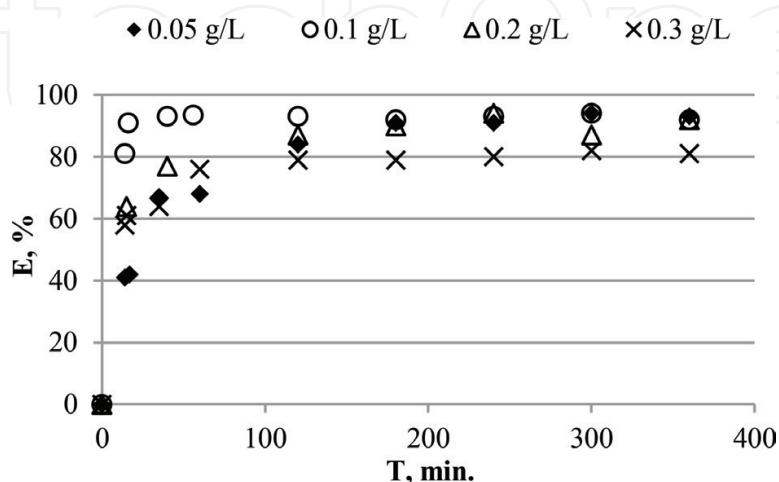


Figure 9. Efficiency of the extraction of uranium in the membrane contactor depending on the initial concentration of uranium in the feed solution.

upscaling, etc. However, some drawbacks also exist, among others concentration polarization and fouling [39]. There is also the risk of wetting the membranes during long-term operation of the module resulting in mixing of the two phases. For the proper operation of membrane contactors, it is important to maintain appropriate hydrodynamic conditions for flow of solutions over the membrane surface in order to eliminate such unfavorable phenomena.

5. Tentative economic analysis

In the case of low-grade uranium ores it is important to carry out a detailed geo-economic analysis, which will be aimed at reliable estimation of the cost of ore extraction. The costs of further technological processes of uranium recovery from the extracted ore in the initial phase are less important, because they can be very different, taking into account technological progress. While the cost of the mine construction and extraction of rocks on the surface, even in the long term, are not subject of significant changes.

In the case of the so-called Rajsk deposit, detailed geological and geochemical data were available. This allowed the development of a detailed mine model. Moreover, because the structure and form of uranium concentration of Lower Ordovician dictyonema Shales are similar to the Zechstein copper deposits exploited on a large scale on the Fore-Sudetic Monocline, there was a possibility to apply current costs of mining excavations, machinery and equipment as well as human labor.

In developing the model of mine adopted a number of assumptions resulting from the analysis of geological data and technology as well as the assumed concept of mining operation.

The deposit has an area of 16 km², occurs at a depth of 400 to 550 m, the average thickness of the uranium-rich rocks is 2.88 m, and the average uranium content is 69 ppm. Recovery of uranium from the ore was assumed at 65% [12]. Based on these parameters of deposits, it was assumed that the operating time of the potential mine will be 24 years, with an annual production capacity of the mine about 4 million Mg/year, which will allow uranium mining about 270–300 Mg per year, and taking into account the uranium recovery from the ore will allow the uranium production of approximately 200 Mg/year [40]. This quantity is necessary for the operation of 1 GWe nuclear power plant.

Taking into account all the above assumptions, it was calculated that the cost of extraction of the ore needed to production of 1 kg yellow cake (commercial product of uranium) will be about \$ 800. This cost does not include the cost of technological processing of the ore, which will be quite high due to the low uranium content in the ore and its occurrence mainly in the form of organometallic compounds, which significantly reduce the uranium recovery. To assess the economic value of this occurrence of uranium ore, it should be compared to the price of a commercial product on the world market. Historically, the highest price of yellow cake at the turn of 2007/2008 was around \$ 175/kg and was extremely speculative. The price of this product in 2015 was about \$ 80/kg. The developed model of the exploitation of the deposit and based on it the evaluation of the cost of obtaining uranium ore from Lower Ordovician dictyonema shale (Podlasie Depression) justifies the statement of unprofitable extraction of uranium from this rock formation in a very long time perspective [3].

6. Environmental impact and radiation protection connected to uranium production in Poland

Radiation protection aims at protecting the health and life of humans and animals as well as protecting the environment from the harmful effects of ionizing radiation. Working with uranium is associated with the risk of exposure to ionizing radiation. In order to reduce the risk to a reasonable minimum, strategies and rules for radiological protection have been introduced worldwide. Radiological protection is largely based on the recommendations of three institutions: the International Commission for Radiation Protection (ICRP), the International Atomic Energy Agency (IAEA) and the Euratom Directives. Usually, the guidelines described in the publications of these institutions are implemented in the law of each country.

Of the various uranium isotopes, U-238 is the most common, accounting for 99.3% of uranium in the earth's crust. U-238 is the beginning of a uranium series of decay chain consisting of 15 radioactive elements with different half-life and terminating with Pb-206 permanent lead isotope. The radioactivity associated with uranium corresponds not only to uranium but also to a greater extent to its decay products and, in particular, to the noble gas radon (Rn-222). It should be emphasized that radiation exposure from uranium and its derivatives is considered natural and present in every corner of the earth. Radon exposure is the largest part of the effective dose received from the environment by a statistical person in Poland and it approximately equals 1.36 mSv/year [41]. Isotopes from the uranium decay series emit both α and β particles. During α -decay, γ -radiation is also emitted. From the radiation protection point of view matter both the type of emitted radiation and the physical form of the emitter. The α radiation is 20 times more effective than the β or γ radiation, but its penetration is small—it is completely retained by a sheet of paper or skin. Generally, the α radiation is not harmful to health as long as the emitter does not get inside the body. This happens mainly through drinking water or—in the form of dust, aerosol or noble gas—transferred to the lungs. The γ -radiation has a greater penetrating power than β -radiation and can therefore be an important component of the absorbed dose.

Uranium is being mined in many parts of the world because it is a basic element used as a fuel for nuclear power and for military purposes. Radiation protection refers to uranium at each stage of the fuel cycle: from ore extraction, milling, to yellowcake (triuranium octoxide) production, further enrichment, fuel elements production, fission reaction at power plants for processing, to storage and disposal of spent fuel.

From the late 1940s to the 1970s, in Poland, uranium ore was mined and processed in Lower Silesia. The ore was extracted by the classical method—the material was brought out from the underground to the surface and collected in heaps [3]. The uranium ore was then split to the rich ore, the poor ore and the gangue rocks [42]. The rich ore went directly to the Soviet Union. The poor ore was enriched on site and the resulting concentrate was exported to the Soviet Union. Mining and reprocessing of uranium was performed by the “Kowary Mines. State-owned Extraordinary Enterprise,” based in Kowary, later renamed “R1 Industrial Plant.” At that time, probably no radiological protection standards were met, and miners may not exactly know what they were extracting and how it could affect their health.

There are a number of uranium ore mining sites in 13 locations at Lower Silesia: heaps with varied concentration of uranium ore—the highest values up to 2000 ppm, open shafts, mine

tunnels, and sedimentation ponds [43]. Most shafts and tunnels are protected against unauthorized entry. So far, almost no attempts have been made to reclaim these areas. Exceptions are reclamation of the sediment tank in Kowary and the protection of some dumps being washed by water [44]. This area is covered by radiation monitoring of the National Atomic Energy Agency (PAA) as an area with increased levels of ionizing radiation from naturally occurring radioactive materials as a result of human activity [for example, see [41, 45]]. The monitoring consists mainly of investigating the α and β total activity and the level of radon in drinking water and mining effluents—60 measuring points, measuring gamma radiation dose in air (62 measurement points) and radon concentration in air. Measured levels in drinking water do not exceed the reference levels specified in the recommendations of the World Health Organization Guidelines for drinking-water quality, Vol. 1 Recommendations. Geneva, 1993: 100 mBq/dm³ for total α activity and 1000 mBq/dm³ for total β activity. These levels are often exceeded in mined water. As far as radon is concerned, the activity happens to exceed the limit of 100 Bq/dm³, which is acceptable for drinking water points established by the EU Directive 2013/59/ EURATOM and for water from excavation can exceed 700 Bq/dm³. Despite this, the PAA's annual reports state that "although water from mining excavations, surface water and groundwater are not intended for use as drinking water and do not present a direct health risk, they should continue to be systematically monitored for their increased radioactivity" and "generally speaking, even in this region of Poland, with the highest possible risk from radon and from natural radioactive elements in the soil, this threat to the local population is negligibly small" [41]. The PAA reports lack of information about the increased radioactivity of uranium heaps. Meanwhile, research carried out under the Strategic Research Project, "Technologies supporting the development of safe nuclear power" in 2010–2012 by a consortium led by the University of Warsaw showed elevated levels of radiation and elevated uranium in the soil in many places (among other uranium heaps in Lower Silesia) in Poland. The authors suggested that such places should be labeled, and preferably fenced [46].

The possible impact of uranium heaps on the environment is further taken into consideration. This can happen through water erosion of heaps and migration of heavy metals, including uranium and radium isotopes to groundwater and underground waters, and to soils in the area. Increased uranium content and radioactivity were observed in river beds flowing from these areas, even up to 20 km from the heaps (e.g. Jedlica river) [44]. Uranium, radium and associated heavy metals can spread and accumulate in organisms—through the food chain. The elevated level of radionuclides possibly increases the natural radiation dose to organisms. It seems that the harmfulness of uranium for organisms is not determined by its radioactivity, but rather by its chemical toxicity and that of the other accompanying heavy metals. So far, there has been no systematic study aimed to determine how uranium concentrations and elevated background radiation affect the individual organisms and ecosystems.

Lower Silesia is not the only area where elevated uranium level can have an impact on the environment. Uranium is also abundant in the material deposited on heaps after copper mining in Legnica-Głogów Copper District or on heaps formed after the production of phosphoric acid and phosphate fertilizers in Police, Wizów and Wiślinka near Gdańsk [47]. Radiological risk in these places should be considered negligible. The threat to the environment probably is related to other heavy metals and elements rather than to uranium.

From the point of view of radiation protection and environmental impact, the uranium industry in Poland does not cause any major threat. Uranium mining and processing activities were completed 40 years ago—at present, there is no nuclear power industry or military technology related to uranium. There are uranium mine residues in Lower Silesia, and there is an increase in the levels of ionizing radiation caused by human activity associated with uranium, but there is no evidence of a radiological hazard to humans or a significant environmental hazard connected to it.

7. Conclusion

The characteristics of Polish low-grade uranium resources were presented in the paper.

The set of methods and technology scheme that could be implemented to extract uranium from low-grade ores and other raw materials were shown. Uranium can be recovered with high efficiency by solid–liquid extraction (almost 100% efficiency), followed by liquid–liquid extraction or/and ion exchange methods. The synergistic mixture of DEHPA and TBP (0.2 M:0.2 M) together with $(\text{NH}_4)_2\text{CO}_3$ as a stripping agent were found as a good route for uranium recovery (99% of yield). The study of the precipitation of yellow cake in different forms, e.g. $(\text{NH}_4)_2\text{U}_2\text{O}_7$ and $\text{UO}_4 \cdot \text{H}_2\text{O}$, was carried out with high efficiencies reaching 98%. The simultaneous recovery of other valuable metals, such as lanthanides, could improve the economics of proposed technology.

The studies performed revealed the feasibility of the proposed technology; however, its profitability in the current uranium supply could be questioned. The environmental impact and related risk from uranium mining and processing in Poland were discussed.

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