



Dictyonema black shale and Triassic sandstones as potential sources of uranium

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Abstract. The main objective of the present study was an assessment of the possibility of uranium recovery from domestic resources in Poland. In the first stage uranium was leached from the ground uranium ore by using acidic (sulfuric acid or hydrochloric acid) or alkaline (carbonate) solutions. The leaching efficiencies of uranium were dependent on the type of ore and it reached 81% for Dictyonemite shales and almost 100% for sandstones. The novel leaching routes, with the application of the helical membrane contactor equipped with rotating part were tested. The obtained postleaching solutions were concentrated and purified using solvent extraction or ion exchange chromatography. New methods of solvent extraction, as well as hybrid processes for separation and purification of the product, were studied. Extraction with the use of membrane capillary contactors that has many advantages above conventional methods was also proposed as an alternative purification method. The final product U_5O_8 could be obtained by the precipitation of 'yellow cake', followed by calcination step. The results of precipitation of ammonium diuranate and uranium peroxide from diluted uranium solution were presented.

Key words: uranium ores • leaching • extraction • ion exchange chromatography • precipitation

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Introduction

In January 2014, The Government of Poland adopted the Program of Polish Nuclear Energy [1]. According to this program the first nuclear power reactor will be put into operation around the year 2025, and the second one in 2030. One of the basic issues of this Program is to ensure the safety of nuclear fuel supply for future Polish nuclear reactors. Presently, the mining of Polish low-grade uranium ores is unprofitable. However, studies on the prospects of recovery of uranium from domestic resources are in progress, keeping in mind the inevitable growing uranium demand and perspectives of the changes in global uranium market.

According to OECD-NEA Red Book (2014) [2] identified conventional uranium resources in Poland count 7270 T; historical research led to the determination of 20 000 T of speculative resources.

Nevertheless, these data concerns information from old geological documentations, which do not fulfill current economic conditions. Recent reinterpretation of geological data made in 2009–2010 [3, 4] shows that Poland has not identified conventional resources profitable to manage. Without more precise exploration of those resources, there would appear to be no possibility for profitable exploitation.

The uranium mineralization in Poland occurs in the Lower and Middle Triassic sandstones of the central part of Peribaltic Syncline, where the maximum U content exceeds 1.5% (Fig. 1). Uranium concentration in Lower Ordovician Dictyonema shale is related to the organic-rich black shale formation with low content of uranium ranging from few tens up to about 250 ppm. These two uranium-bearing geological formations, significantly different in terms of the origin and forms of occurrence of uranium, were taken into consideration in the present studies on the possibility of fuel production for nuclear power plant in Poland. The project realized by the Institute of Nuclear Chemistry and Technology concerns the development of effective technology for uranium extraction from low-grade indigenous ores leading to obtain yellow cake.

Materials and methods

Geological-mineralogical characterization

According to assessments done by Polish Geological Institute apart from well-known resources in Sudetes exploited in 1948–1973, the other deposits of uranium are in Podlasie Depression (northeast Poland) and the central parts of Peribaltic Syncline [4]. The deposits in the Sudetenland deemed to be exhausted; they were evaluated in the 70s of the twentieth century. Current project focused on shales of the Podlasie region and sandstones of Peribaltic Syncline.

Dictyonema shale of Podlasie Depression

Uranium mineralization is associated with a layer of strongly diagenous, dark Dictyonema shales, Lower Ordovician age, with a thickness from several centimeters to 4 m (average thickness of about 2.7 m). Profile contains a series of black shales (1.0–1.5 m), passing upward in brown shales, replaced above by the light beige shales with phosphates (about 5 cm thick) [4]. This rock formation is almost flat and is weakly disturbed faults. Uranium occurs mainly in the black shales. Geochemical background in black shales is about 70 ppm U. In addition to uranium in black shales relatively high concentrations of vanadium (100–2000 ppm) and molybdenum (from a dozen to 500 ppm) were found. In brown shales, background uranium content is twice as lower, and vanadium even tripled. Typical distribution of uranium and accompanying metals is presented in Fig. 1C. Low uranium content while a high content of organic matter (from a few to more than 10% of total organic carbon (TOC)) causes not observed its own uranium minerals. Uranium is probably in the form of organometallic compounds. The depth of occurrence changed from 400 m in the north-eastern part of Podlasie Depression up to 1000–1200 m in western and southern parts of this structure. Based on data from dozens of boreholes spaced on the surface of 840 km², which document the existence of a layer enriched in uranium to a depth of 800 m, uranium reserves estimated at 88 850 T. This is 'black

shale' type of uranium mineralization, known from Sweden (Upper Cambrian Alum shale), Estonia and St. Petersburg vicinity (Dictyonema shale). The advantages of uranium mineralization in this geological formation are: stability for large areas of mineralization and simple geological structure of ore-bearing formation. The disadvantages are: the depth of occurrence, low uranium content and strong uranium-organic matter, which implies technological difficulties in the recovery of uranium.

Triassic sediments of Peribaltic Syncline

Uranium mineralization in Triassic rocks of the Polish Lowland occurs in form of several levels [4]. The most interesting uranium-rich rocks have been found in the middle part of Peribaltic Syncline (East of Gdańsk) in the rocks of Upper Bunter. These concentrations represent sandstone type uranium mineralization. The richest mineralization, associated with fine-grained, grey and green-grey, slightly diagenous sandstones, occurs on the Vistula Spit. In a single hole in a horizon thickness of 4.43 m weighted average uranium content is 0.26%. In individual samples the uranium content reaches 1.5%. Uranium is accompanied by high content of V, Se, Mo, Pb, As (Fig. 1B). Mineralogical studies showed the presence of coffinite and nasturan as well as pyrite, galena and clausthalite. Two ore bodies were identified on the Vistula Spit. They have

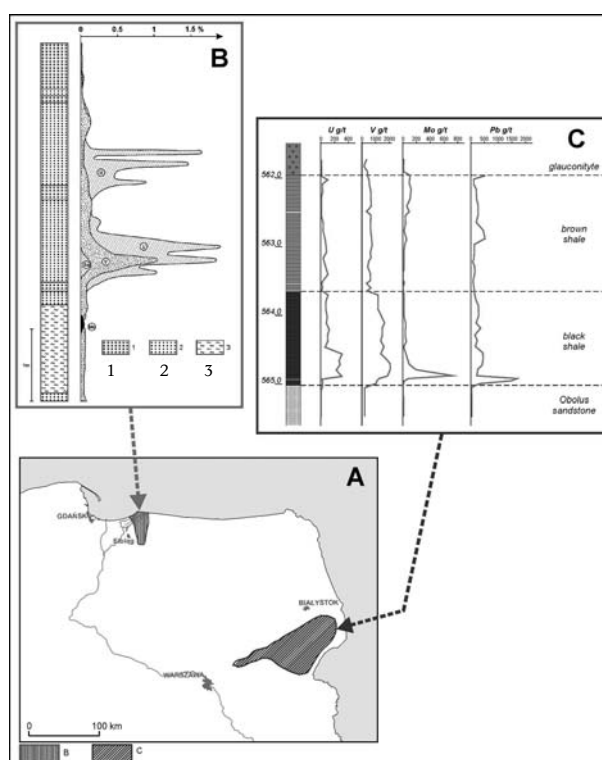


Fig. 1. Fig. 1A. Location of uranium-bearing formations in Poland: B – Triassic sediments of Peribaltic Syncline; C – Lower Ordovician Dictyonema shales. Fig. 1B. Distribution of uranium and accompanying metals in profile of uranium-bearing sandstone formation (Peribaltic Syncline): 1 – conglomerates, 2 – sandstones, 3 – mudstones. Fig. 1C. Distribution of uranium and accompanying metals in Lower Ordovician Dictyonema shales.

Table 1. The content of selected metals in Polish uranium ores

	Dictyonema shales [ppm]	Triassic sandstones [ppm]
U	41–215	4–1316
Th	6–15	2–82
Cu	142–620	14–111
Co	<10–80	3–163
La	31–62	4–53
V	805–2050	37–770
Yb	0–7	0–5
Mo	10–270	0–9
Fe	11 500–78 900	3700–180 000

probably the form similar to the ‘tabular’ type [4]. The depth of ore bodies on the Vistula Spit area is from 750 to 800 m. To the south of the Vistula Lagoon the presence of mineralization was found in several boreholes and the depth of occurrence is about 950 to 1170 m. The uranium concentrations are several times lower and only in single samples of sandstones exceed 1000 ppm.

Chemical characteristics of investigated material

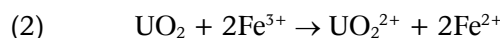
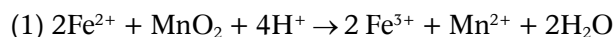
The material originating from uranium ores vary significantly from deposit to deposit. The analysis of uranium concentration showed the big diversity of uranium concentration in the vertical profile: from 41 ppm to 215 ppm for Dictyonema shales and from 4.2 ppm (in non-mineralized host rocks) to 1316 ppm for the Triassic sandstones. In the ores uranium usually was 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 [5]. The average content of selected metals in uranium ore samples are specified in Table 1.

Treatment of uranium ores

The effect of ore mineralogy and mineral liberation on the leaching behavior of uranium is not well defined. For this reason the procedure of uranium extraction should be designed to fit to specific characteristics of its ores, however, the general process is similar for most of them. The basic steps of processing of uranium ores are crushing and grinding, leaching, solid-liquid separation, ion exchange, solvent extraction, and precipitation to obtain final product yellow cake – U₃O₈ (Fig. 2) [6].

At the start of the processing of uranium, mined ores were crushed and grinded to produce a grain size less than or equal to 0.2 mm to increase the surface area exposed to leaching. Then the ores were leached from the ground ore by using acidic (sulfuric acid or hydrochloric acid) or alkaline (carbonate) solutions [7, 8]. The oxidizing agent (KMnO₄, MnO₂, or H₂O₂) to oxidize all uranium to U(VI) form, was added. However, the uranium oxidation requires the presence of ferric ion, regardless of used oxidizing

agents [6]. The oxidizing agent oxidizes ferrous ion to ferric ion that is oxidizer the uranium as shown by Eqs. (1) and (2)



The Dictyonema shales are more difficult to uranium leaching than sandstones because uranium is closely associated with organic matter. For this reason the calcination of Dictyonema shales prior to the leaching process was necessary. The samples of sandstones that contained less organic matter (below 0.1%) were not pretreated in the oven. The postleaching solution was separated from the ores residue. The concentration of uranium and other elements in postleaching solution was determined using ICP-MS analyses [9].

Uranium and other metals can be recovered from postleaching solutions by ion exchange [10] or solvent extraction [11, 12] followed by stripping to aqueous phase [13, 14]. The chemicals and reagents used in this study were analytical or reagent grade. Basic anion exchanger (Dowex1 X8, 200–400 mesh) and acidic cation exchanger (Dowex50 WX8, 200–400 mesh), the extracting agents: tributylphosphate (TBP), di(2-ethylhexyl)phosphoric

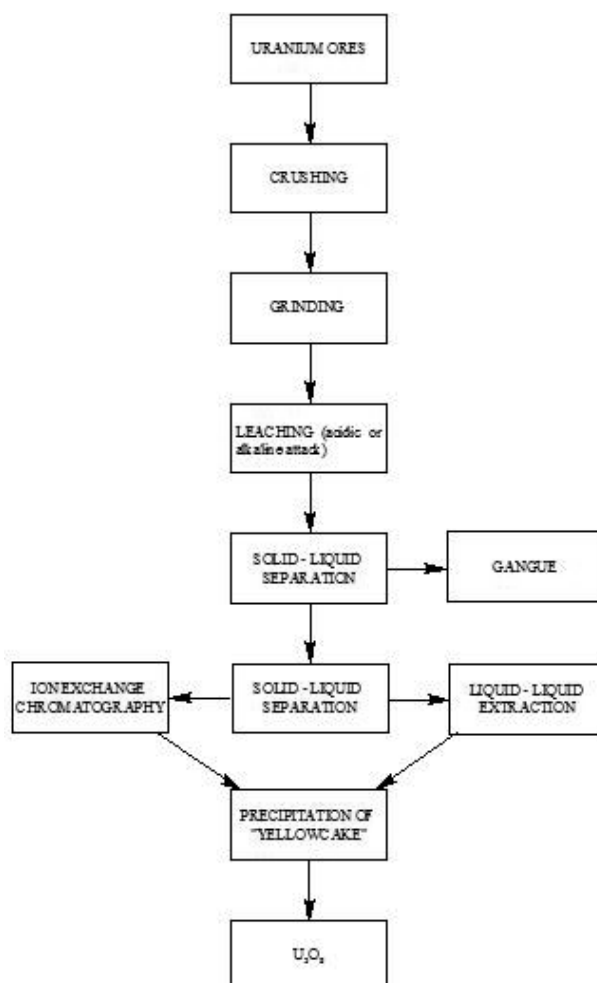


Fig. 2. Treatment of uranium ores.

acid (D2EHPA), trioctylphosphine oxide (TOPO), triethylamine (TEA), tri-*n*-octylamine (TnOA) and kerosene were supplied by Sigma-Aldrich. The study of the precipitation was carried out with the model solution of uranium that was prepared by dissolving a fixed amount of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 2 M sulfuric acid. Uranyl nitrate was supplied by Chemapol Praha. The ammonium solution, concentration of 25% (POCH, Gliwice) was used for precipitation of ammonium diuranate.

Results and discussion

Leaching uranium ores

The solid-liquid extraction is a very important stage in the technology of uranium production from the uranium ores. In the present work at the beginning of the extraction process, uranium was leached from the ground ore by solid-liquid extraction using sulfuric acid or carbonate (CO_3^{2-}) solutions. The content of metals in postleaching solution can vary depending on the initial composition of the rock and the procedure of extraction applied. Interpretation is rather difficult because as was said earlier, the effect of ore mineralogy and mineral liberation on the leaching behavior of uranium and other metals is not well defined. The experimental work showed that sandstones were more readily leachable in comparison with the Dictyonema shales. The best results of acid leaching of Dictyonema shales were found for leaching with 10% H_2SO_4 during 8 h at 80°C. The average efficiency of uranium leaching from different ore materials was in the range of 64–81%. The leaching efficiency of other metals was as follows: 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%. The alkaline leaching (5% $\text{Na}_2\text{CO}_3/5\%$ NaHCO_3 or 8% $\text{NaOH}/18\%$ Na_2CO_3) was more selective in respect of uranium than acidic leaching. In alkaline postleaching solutions only three or two metallic components of the ores were detected: U, Mo and V (Dictyonema shales) or U and small amounts of V (sandstones). In the case of sandstones, 57–92% of uranium and 2–22% of vanadium were leached with a mixture of sodium carbonate and bicarbonate. In the case of calcinated samples of Dictyonema shales the uranium was extracted with 42% efficiency, molybdenum with 24% and vanadium with ca. 8% efficiency. The comparison of uranium leaching efficiencies depending on lixiviant and leaching method is presented in Figs. 3 and 4.

One of the stages before further processing is solid-liquid phase separation. These two processes: leaching and separation could be conducted in one apparatus with the use of the membrane contactor with Couette–Taylor helical flow (Fig. 5) [15].

The suspension of uranium ores in leaching medium is transferred to the membrane contactor where



Fig. 3. 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% $\text{Na}_2\text{CO}_3/5\%$ 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 – sintering process with addition of 10% NaCl at 840°C during 3 h, than leaching with 5% H_2SO_4 , MnO_2 , 80°C, 8 h.

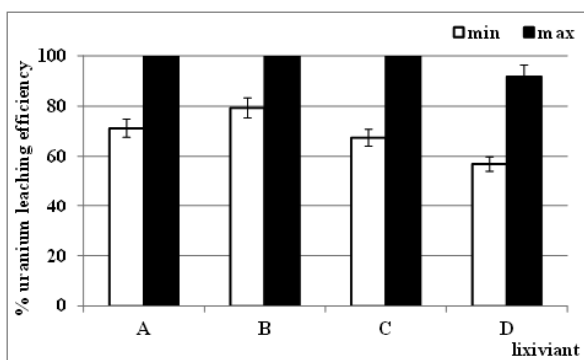


Fig. 4. Efficiency of leaching uranium from sandstones by various lixiviants, liquid/solid ratio of 8:1 (vol./wt basis), A – 10% H_2SO_4 , oxidizing agent: MnO_2 , 60°C, 1 h; B – 10% HCl , oxidizing agent: 30% H_2O_2 , 60°C, 1 h; C – 8% $\text{NaOH}/18\%$ Na_2CO_3 , oxidizing agent: 30% H_2O_2 , 60°C, 1 h; D – 5% $\text{Na}_2\text{CO}_3/5\%$ NaHCO_3 , oxidizing agent: KMnO_4 , 60°C, 1 h.

leaching process and separation of postleaching solution from the concentrated suspension of gangue were conducted. Studies included determination of the leaching process efficiency depending on velocity of the feed flow as well as rotation frequency of rotor. The process parameters varied according the experimental plan: the velocity of the feed flow (Q_s) in range of 0.67 to 1.33 L/min, and rotation frequency of the inner cylinder (Ω) in the range from

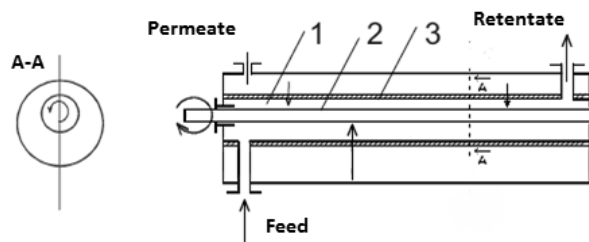


Fig. 5. Membrane contactor. 1 – space with a Couette–Taylor flow, 2 – rotor, 3 – metallic tubular membrane.

Table 2. Uranium leaching efficiencies in the helical membrane contactor in comparison with results obtained in stationary reactor

Ω [rpm]	Leaching efficiency [%]	
	$Q_s = 0.67$ l/min	$Q_s = 1.33$ l/min
0	49 ± 2	66 ± 3
1000	55 ± 3	69 ± 4
1500	54 ± 3	57 ± 3
2500	64 ± 3	64 ± 3
Stationary	72 ± 4	

0 rpm to 25 000 rpm. The transmembrane pressure was maintained constant of 50 kPa. The experiments were performed at ambient temperature. Results of experiments are presented in Table 2.

It can be noticed that by increasing flow velocity the efficiency of uranium leaching can be enlarged but the influence of the speed of the rotor is rather insignificant. The effectiveness of uranium leaching was compared to results obtained from leaching process conducted in conventional manner, in stationary reactor at 80°C. The advantage of using the membrane contactor is a possibility of combining two processes in one apparatus: leaching and separation of solid phase from postleaching solutions and conducting the leaching process in lower temperature. Such an approach results in reduction of total cost of operation with no consequences to the separation efficiency.

Concentration and purification of uranium solutions: liquid-liquid extraction and stripping process

In the next step the postleaching solution was concentrated and purified by liquid-liquid extraction or ion exchange. The extracting agents, like TBP, DEHPA, TOPO, TEA, TnOA, and other reagents, were tested with the model uranium solutions. The mixture of DEHPA and TBP (0.2 M:0.2 M) was found as a good extractant for uranium and the studies of extraction of uranium from leaching liquors (sulfuric and carbonate) were carried out. At the beginning of extraction process, the alkaline postleaching solution was acidified with sulfuric acid to pH 1. The use a different reagents as strip solutions for uranium in organic phase was also investigated. The obtained results were satisfying; the summarized yield (%R) of extraction (%E) and stripping (%S) reached even 98%. For this process apart from uranium, the other elements were also examined. The extraction/stripping processes of alkaline and acidic postleaching solutions are reported in Tables 3 and 4, respectively. The separation of uranium from accompanying metals from acid leaching solution was only partial. Uranium was recovered with high efficiency but the final solution was contaminated by iron and small amounts of other metals: vanadium and ytterbium. It is worthy to notice that the separation of uranium from alkaline postleaching solution was almost complete (Table 4). The extraction, followed by stripping step gave pure uranium solution.

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

Metal	Postleaching solution			Extracting phase			Stripping phase 0.5 M (NH ₄) ₂ CO ₃			Stripping phase 0.5 M Na ₂ CO ₃		
	C_a [ppm] ^{a)}	C_b [ppm] ^{b)}	%E	C_c [ppm] ^{c)}	%S	%R	C_d [ppm] ^{c)}	%S	%R			
U	25	25 ± 1	100	25 ± 1	99	99	25 ± 1	99	99			
Th	<1	–	–	–	–	–	–	–	–			
Cu	14	0	0	–	–	–	–	–	–			
Co	<1	–	–	–	–	–	–	–	–			
Mn	27	0	0	–	–	–	–	–	–			
La	<1	–	–	–	–	–	–	–	–			
V	3	<1	–	–	–	–	–	–	–			
Mo	<1	–	–	–	–	–	–	–	–			
Yb	<1	–	–	–	–	–	–	–	–			
Fe	230	74 ± 7	32	21 ± 2	28	9	24 ± 2	32	10			

^{a)} C_a – concentrations of metals in postleaching 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 4. Extraction and stripping efficiencies of metals from alkaline postleaching solution, [DEHP]:[TBP] 0.2 M:0.2 M, temperature: 22°C, pH 1, phase ratio (organic/aqueous) 1:1

Metal	Postleaching solution			Extracting phase			Stripping phase 0.5 M (NH ₄) ₂ CO ₃			Stripping phase 0.5 M Na ₂ CO ₃		
	C_a [ppm] ^{a)}	C_b [ppm] ^{b)}	%E	C_c [ppm] ^{c)}	%S	%R	C_d [ppm] ^{c)}	%S	%R			
U	20	20 ± 1	100	20 ± 1	99	99	20 ± 1	99	99			
V	<1	–	–	–	–	–	–	–	–			
Mo	<1	–	–	–	–	–	–	–	–			

^{a)} C_a – concentrations of metals in postleaching solution.

^{b)} C_b – concentrations of metals in organic phase from extraction process.

^{c)} C_c , C_d – concentrations of metals in stripping phase.

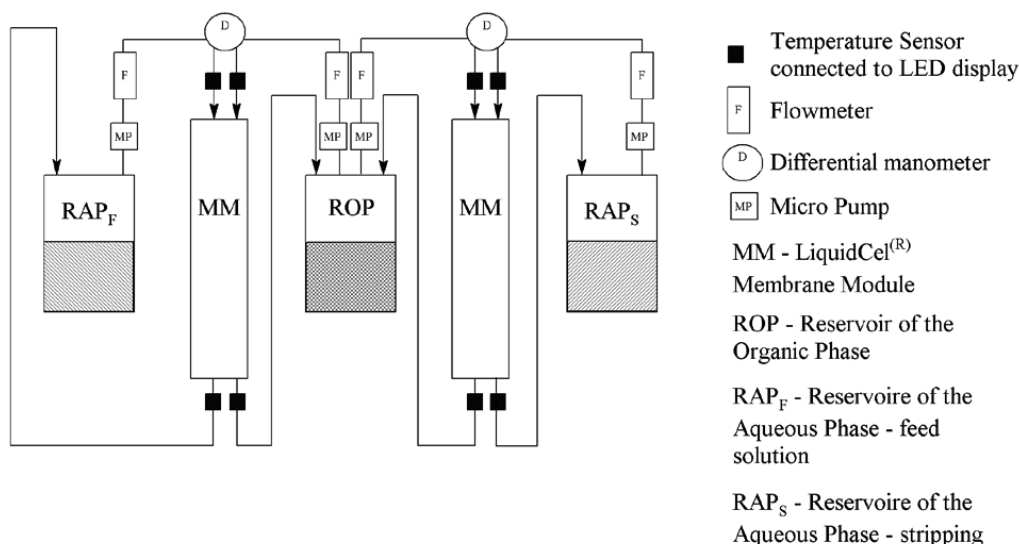


Fig. 6. The scheme of the installation for membrane extraction of uranium.

In the present work alternative approach for liquid-liquid extraction that based on the membrane process and application of membrane contactors [16] is proposed. As a standard apparatus for liquid-liquid extraction a multistage mixer-settler arrangement with concurrent flow of two phases – aqueous and organic, is used. The system was fitted with devices, which measure the parameters and control the process (Fig. 6). The membrane applied in the contactor does not offer any selectivity for a particular species with respect to another. It simply acts as a barrier between two phases involved, by allowing their contact throughout a precisely defined interfacial area. Two phases are separated by the membrane and species are transferred from one phase to another by only diffusion.

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

The results obtained in extraction experiments with applications of membrane contactor are similar to these that were obtained in conventional extraction experiments.

Concluding the results of experiments, it is worthy to mention that such metals like Zn, Cr, Sb that are present in the ores were removed at the leaching stage. The using extraction and stripping processes allows to remove some metallic components from postleaching liquors like thorium and copper. Further purification and separation of uranium from other metals could be performed by ion exchange chromatography or a sequence of ion exchange/extraction treatments.

Ion exchange chromatography

The ion exchange is a very effective method used for the separation of metals. In presented study, two following ion-exchange columns, one by one,

were adapted for purification of acidic postleaching solutions. First column was filled with strongly basic anion exchanger (Dowex1 X8) and the second one with strongly acidic cation exchanger (Dowex50 WX8) (Fig. 7).

Feed solution was introduced into the first column. Cations were not adsorbed and were eluted to the second column. Uranium, vanadium, and molybdenum complexes were adsorbed in the first column and in the next step they were eluted with 0.15 M H_2SO_4 , followed by 1 M sulfuric acid. The first eluent removed the vanadium complex from the column. The using of 1 M H_2SO_4 allowed to obtain fraction of uranium compounds. The molybdenum is very strongly fixed in anion exchange column and it can be eluted partially by strong acid as 1 M H_2SO_4 .

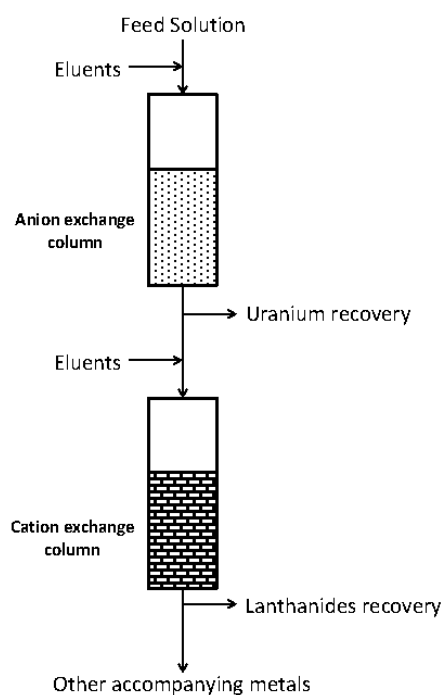


Fig. 7. Set of two columns with strongly basic anion exchanger (Dowex1 X8) and strongly acidic cation exchanger (Dowex50 WX8).

Table 5. The precipitation of uranium compounds from solution of $\text{UO}_2(\text{NO}_3)_2$ in 2 M H_2SO_4

Uranium compound	U [mg/mL]	Temperature [°C]/Time [h]	Yield [%]
$(\text{NH}_4)_2\text{U}_2\text{O}_7$	0.3	40°C/4 h	88
	0.5	40°C/4 h	98
$\text{UO}_4 \cdot \text{H}_2\text{O}$	1.0	90°C/4 h	99

For this reason the uranium fraction from liquors from leaching of black shales can be contaminated with molybdenum. In another way the purification of liquors from leaching of sandstones that does not contain molybdenum gave a pure uranium fraction. The efficiencies of recovery of metals was almost quantitative: 95–98% for uranium, 100% for lanthanum, 95–98% ytterbium. Other metals were not separated and were present in effluent from columns.

Yellow cake precipitation

Uranium present in acidic or alkaline solution produced by the ion exchange chromatography or solvent-extraction processes described above is typically precipitated as polyuranate. This precipitation is the most crucial stage in the production of yellow cake. It is followed by calcination step in which U_3O_8 is formed. In the present work, the precipitation of two different forms of yellow cakes: $(\text{NH}_4)_2\text{U}_2\text{O}_7$ and $\text{UO}_4 \cdot \text{H}_2\text{O}$ was carried out from the model uranium solution. The influence of temperature and concentration of uranyl ions in the solution were examined. The representative results are presented in Table 5. It is significant that ammonium diuranate was precipitated from solutions containing low concentration of uranium (0.3–0.5 mg/mL).

Conclusion

The solid-liquid leaching efficiencies of uranium and accompanying metals from Polish ores vary in a broad range, however for some samples they reached almost 100%. Very interesting results, in terms of selectivity and efficiencies of leaching were obtained in the process of leaching with alkaline solutions. The purification of uranium from accompanying metals was achieved by the ion exchange chromatography or solvent-solvent extraction with satisfied results. The effective precipitation of uranium compounds, precursors of U_3O_8 was carried out.

The present studies allowed preparing the set of methods and technology that could be implemented to extract uranium from Polish ores and other sources. Based on the results of the experiments a conceptual design for the further construction of pilot plant, producing yellow cake was developed [17]. The project was completed with technical and economic analysis [18] done for the pilot plant of capacity 100 kg/day. The results of the pilot studies will allow the assessment of the proposed flow sheet, and will provide information on the optimum operation of individual devices and preparation of the data used to build the full industrial scale facility.

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