

Extraction of uranium from low-grade Polish ores: dictyonemic shales and sandstones

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Abstract. Leaching studies were performed to develop a suitable method for extraction of uranium from domestic uranium ores: dictyonemic shales and sandstones. The extracting procedure was composed of successive separation steps: crushing and grinding, acid or alkaline leaching, solid-liquid separation, and inductively coupled plasma mass spectrometry (ICP-MS) analyses of post-leaching solutions. The influence of such process parameters as temperature, pressure, particle size of solid material, kind of leaching solution and its concentration, on the recovery efficiency of uranium and accompanying metals were tested. The efficiency of uranium leaching with sulphuric acid solution achieved 81%. Satisfactory results were obtained for the alkaline leaching process. It was found that uranium can be selectively extracted by the alkaline leaching solution. Almost complete extraction of uranium from sandstones was achieved when a mixture of sodium carbonate and sodium hydroxide, with hydrogen peroxide as a leaching solution was used.

Key words: uranium ores • leaching • dictyonemic shales • sandstones

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Introduction

Nuclear power is one of the branches of power industry, which despite a temporary slowdown caused by the Fukushima an accident, is expected to be developed rapidly next years (reported by Capgemini [24]). Inevitable development of nuclear power in Poland implies an interest in checking the possibility of using national resources of uranium to produce fuel [14, 17] for future nuclear reactors.

According to the Program of Polish Nuclear Energy prepared by the Government Commissioner for Nuclear Power, the first nuclear block should be put into operation by the year 2020, and the second around 2030 [17]. The implementation of the Program of Polish Nuclear Energy will include suitable provisions for the assessment of domestic uranium ores, which may be considered as a possible reserve of raw material to produce fuel for Polish reactors. However, the possibility of their practical use should be considered not only in the context of technological feasibility, but also in reference to the global situation on the uranium market.

Global uranium demand is expected to grow up in the next years due to accelerated growth of nuclear power. Additional production based on yet-to-be-

-discovered resources is required to assure security of supplies. In Poland, there are only low-grade uranium ores, with no practical importance. However, it is known that a very profitable ore mines operate at the content of 300 ppm (e.g., Rossing in Namibia), and even 126 ppm (Trekopje in Namibia). Although the present exploitation of Polish uranium deposits has no economic significance, the situation could change in the future with further development of nuclear energy and with exhausting world resources of uranium. These and similar predictions drive many laboratories in the world to initiate studies on the prospects of recovery of uranium from secondary sources, such as sea water [4, 5] or fly ash [25]. The possibility to retrieve uranium from fly ash was studied at the Institute of Nuclear Chemistry and Technology in the 90-ties of the XX century [7, 8].

In the period of 1948–1973, in Poland, uranium was mined in Sudetes (Kowary, Podgórze, Radoniów, and Kopaliny-Kletno) [16, 26] and the Holy Cross Mountains (“Staszic” Mine, Rudki) [2]. About 800 tons of uranium was mined on the Polish territory and exported to the former Soviet Union. Detailed geological studies carried out to the late 80’s of the last century allowed good recognition of uranium occurrence practically in all lithological structural units of Sudetes. However, due to the low content, widespread fragmentation of mineralization and the strong association of uranium with organic matter, this occurrence presents no economic significance [16]. According to assessments done by the Polish Geological Institute (PIG, Warsaw), the other deposits of uranium are in the Lower Ordovician Dictyonema shale of Podlasie Depression (North-East Poland) with a uranium concentration of 75–250 ppm and the most prospective uranium mineralization on the Polish territory – the Lower and Middle Triassic rocks of the central parts of Peribaltic Syncline, where concentrations reach even 1.5% U (recent analysis of archive samples) [18].

The characteristics of the material originating from uranium ores vary significantly from deposit to deposit. The effect of ore mineralogy and mineral liberation on the leaching behaviour of uranium is not well defined. The procedure of uranium extraction must be designed to fit specific characteristics of the ore; however the general scheme of the process is similar for most of the ore materials. The basic steps of processing of uranium ores are crushing and grinding, leaching, solid-liquid separation, ion exchange or solvent extraction, and finally precipitation of final product yellow cake – U_3O_8 [9].

Uranium is usually extracted from the ores by one of two leaching methods: acidic – with sulphuric acid (H_2SO_4) and alkaline – with carbonates (CO_3^{2-}) [1, 6, 9, 10, 12, 15, 19, 20, 22]. The use of oxidants e.g. manganese oxide, sodium chlorate or hydrogen peroxide, increases the leaching ability of uranium since the hexavalent form of uranium U(VI) is more soluble than the reduced form U(IV).

Acid leaching is the predominant process for uranium recovery from the rocks. Sulphuric acid is used usually because of its low cost and availability. Acid consumption depends on the constituents of ore material. The carbonate materials are the principal acid consumer. Typically, leaching recoveries range from 85 to 95% [6, 9, 12, 15, 20, 22]. The time of leaching varies from several

to more than 24 h. It can be greatly reduced by increasing temperature of process. The leaching rate can be also increased by the application of ultrasounds [1]. The post-leaching solution contains a wide variety of metal ions, e.g. uranium, aluminium, magnesium, vanadium, thorium, iron and copper.

The most common alkaline leaching solution is a mixture of sodium carbonate and sodium bicarbonate [22]. In comparison with acid processing, alkaline leaching has the advantage of being selective for uranium. There are several examples of alkaline process in the literature. Uranium was selectively leached by a mixture of sodium carbonate, sodium hydroxide and hydrogen peroxide from hydrous oxide Egyptian monazite [10]. This method led to obtaining uranium of purity not less than 99%. It is worthy of notice that more than 80% of uranium was leached with the alkaline carbonate solution. On the other hand, the leaching of uranium from the phosphate rock with ammonium carbonate/bicarbonate solution, without oxidizing agent, was not very effective [19]. In this process only 40% of uranium was extracted from the concentrated phosphate rock.

The aim of the present studies was to find a solid-liquid extraction method suitable for separation of uranium from domestic low-grade uranium ores and to evaluate them as potential sources of nuclear fuel. The research work described in the paper covers only the first stage of uranium technology and does not contain final conclusions concerning the viability of the entire venture, which will be possible only after deeper interdisciplinary studies. The authors do not claim either the right to judge on the prospective use of these resources or to decide about adopted fuel cycle options in the future. The studies affect only one of the stages of the technology, although very important for the evaluation of the entire project.

Both leaching methods, acidic and alkaline, were studied to extract uranium from dictyonemic shales and sandstone rocks originating from the boreholes done in domestic uranium deposits. Inductively coupled plasma mass spectrometry analysis was applied to determine the total uranium content in post-leaching solutions. This analytical technique is favourable since it enables to measure directly the mass concentration of total uranium without any chemical separation. It allows also analysing the content of a big variety of other metals that accompany uranium in the ore samples.

Characteristics of ores

The samples of ores for experiments: dictyonemic shales and sandstones were collected from the deposits in Podlasie Depression (Rajsk and Hacki Deposits) and Peribaltic Syncline (Krynica Morska and Ptazskowo Deposits).

The main components of the dictyonemic shales of Podlasie Depression are: quartz, kaolinite, illite, organic and bituminous substances. The dictyonemic shales contain also carbonate minerals as: siderite, dolomite and calcite, as well as sulphides as: pyrite, sphalerite, galenite, marcassite and chalcopyrite. Studies of minerals of Peribaltic Syncline were showed that their main components are coffinite, nasturan, and

Table 1. The chemical composition of the samples^a

| | Dictyonemic shales (%) | Peribaltic sandstones (%) |
|--------------------------------|------------------------|---------------------------|
| SiO ₂ | 38–62 | 22–86 |
| Al ₂ O ₃ | 9–19 | 3–19 |
| Fe ₂ O ₃ | 2.5–7 | 0.8–10 |
| SO ₃ | < 0.01–0.08 | < 0.01–0.56 (2.8 and 2.6) |
| CaO | 0.2–0.5 | 0.5–36 |
| MgO | 0.3–0.8 | 0.4–4.4 |

^aAnalyses were performed by XRF.

sulphides: galanite, pyrite and clausthalite [3, 16]. The chemical composition of the samples of the ores studied was determined in the PIG. The basic components are specified in Table 1.

172 Uranium ore samples from selected boreholes of the mass 100–400 g each, were analysed chemically by ICP-MS, which is nowadays a dominant method for simultaneous analysing of various elements in the sample [11, 13, 21].

The samples represented the material taken from the core of boreholes from Rajsk (Podlasie Depression) and Ptaszkowo (Peribaltic Syncline) selected by geologists and can be considered as representative for these specific areas. The analysis of uranium concentration in dictyonemic shales taken from a single borehole showed a big diversity of uranium concentration in the vertical profile: from 41 to 215 ppm. The concentration of uranium in sandstones from Peribaltic Syncline was higher and reached 1316 ppm. In both types of ores uranium usually was accompanied by other metals, e.g. V, Mo, Th, La, Cu or Co. Some of them, which are valuable and occur in significant concentrations can be recovered in technological process to improve the economy of the whole venture. The results of chemical analysis of uranium ore samples that were selected for further leaching tests, are presented in Table 2. The criterion for selection was the concentration of uranium; however the difference between the samples collected from different boreholes, especially in the case of dictyonemic shales, was not significant. The most intense uranium mineralization occurred in black shales with a high content of organic matter; nevertheless, elevated U concentrations in brown shales were also observed. As a rule, the most of uranium content in the black shales was bound with organic substances, sometimes with clay materials.

Table 2. The content of selected metals in uranium ore samples

| Sample notation | Deposit notation | U (ppm) | V (ppm) | Mo (ppm) | Th (ppm) | La (ppm) | Cu (ppm) | Co (ppm) |
|--------------------|------------------|---------|---------|----------|----------|----------|----------|----------|
| Dictyonemic shales | | | | | | | | |
| 21/10/5 | Rajsk JG-1 | 89 | 1279 | 175 | 10.9 | 36 | 183 | 14 |
| 21/10/8 | Rajsk JG-1 | 121 | 1486 | 296 | 10.9 | 41 | 234 | 20 |
| 21/10/9 | Rajsk JG-1 | 123 | 1359 | 211 | 11.7 | 38 | 192 | 14 |
| 21/10/10 | Rajsk JG-1 | 142 | 1886 | 172 | 12.0 | 35 | 208 | 16 |
| 21/10/22 | Hacki JG-5 | 106 | 1431 | 63 | 10.7 | 40 | 205 | 15 |
| Sandstones | | | | | | | | |
| 21/10/138 | Ptaszkowo IG-1 | 1120 | 142 | < 5 | 4.0 | 14 | 42 | 127 |
| 21/10/140 | Ptaszkowo IG-1 | 1316 | 625 | < 5 | 5.1 | 47 | 28 | 81 |
| 21/10/142 | Ptaszkowo IG-1 | 670 | 770 | < 5 | 4.8 | 29 | 32 | 57 |
| 21/10/160 | Krynica Morska | 565 | 371 | < 5 | 4.3 | 14 | 78 | 96 |

Experiments

ICP-MS analysis

All standard solutions (1 mg/mL) used in ICP-MS analysis were supplied by Perkin Elmer. The following certified reference materials (CRM) were applied in the analysis: Soil 5 (International Atomic Energy Agency – IAEA, Vienna), Lake Sediment SL-1 (IAEA), and Apatite Concentrate CTA-AC1 (Institute of Nuclear Chemistry and Technology – INCT, Warsaw). All reagents were of highest commercially available grade. For grinding of dictyonema shales an agate ball mill (Retsch PM 100) and for sandstones tungsten carbide ring mill (Herzog) were applied. The ICP-MS instrument ELAN DRC II (Perkin Elmer) with a cross-flow nebulizer and with a Scott double-pass spray chamber and Ni cones was used. A muffle furnace with temperature regulation and a recorder (Nabertherm) was applied for fusion.

Representative sample collection by the quartering method has been done. For analysis, 0.5 g samples were weighed and placed in a zirconium crucible; 2 g of Na₂O₂ was added and carefully mixed. The fusion was carried out in a muffle furnace at a temperature of 550°C. The sinter was dissolved in water, then 25 mL of 5 M HNO₃ was added, and the mixture was heated at a temperature of about 80°C to obtain clear solution. Then, the solution was transferred to volumetric flask and adjusted to 250 mL with water. The obtained solutions were diluted respectively with 0.7% HNO₃, and it was added as an internal standard prior to analysis. All samples for analysis were taken in triplicate.

Experimental conditions

It is well established that many factors such as temperature, pressure, particle size, type of leaching solution (acidic or alkaline) and its concentration have a significant effect on the extraction of uranium and the other metals from uranium ores. The influence of all of these factors on the leaching efficiency was examined. In the study, both acidic and alkaline lixiviants were tested as the leaching solutions. Prior to leaching, the samples of dictyonemic shales and sandstones were crushed, divided into four parts and ground in the mill. Then, each sample was classified into five fractions: 0–0.2 mm; 0.2–0.4 mm; 0.4–0.63 mm; 0.63–0.8 mm and 0.8–1 mm. The samples of dictyonemic shales were calcinated at a temperature of 550°C for 4 h in the oven. The samples of sandstones that contained less organic compounds did not need to be pretreated in the oven. The experiments were performed in two experimental set-ups: in a round-bottom glass flask equipped with a back cooler and an agitator in the temperature range of 22–80°C, at ambient pressure, and in an autoclave that allowed adjustment of the parameters in a higher range of temperatures and pressures [23]. The oxidizing agent (MnO₂ or 30% H₂O₂) to oxidize all uranium to U(VI) form was added. The post-leaching solution was separated from the ore residues by filtering and subsequent washing with distilled water. The mass of residue was ~85% of the mass of starting material in the experiment without calcination, and ~78% of the mass of starting material when calcination stage was applied.

Each experiment of leaching was repeated 3–5 times in order to confirm the correctness of the obtained results. The samples of the post-leaching solution were drawn for ICP-MS analysis to estimate the leaching efficiency. The leaching efficiency is defined as the ratio of amount of the metal in post-leaching solution to the amount of the metal in the ore sample according to the formula:

$$E = (m/m_o) \cdot 100\%$$

where: E – efficiency of leaching; m – total mass of the metal recovered in post-leaching solution; m_o – total mass of the metal in the ore sample.

The results of experiments, namely efficiencies of leaching under different process conditions, are presented in Figs. 1–8.

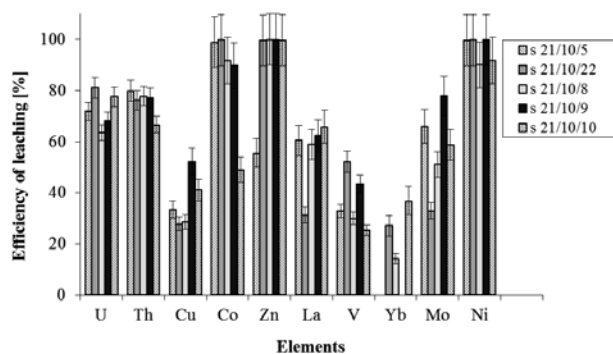


Fig. 1. The efficiency of acid leaching (10% H₂SO₄) of selected elements for five different samples of dictyonemic shales.

Leaching of dictyonemic shales with acidic solutions

Five samples taken from different boreholes, which differed in the content of uranium (89, 106, 121, 123 and 142 ppm), were selected for experiments.

The leaching tests were carried out by using 10% H₂SO₄, at 80°C and ambient pressure, for 8 h.

In Fig. 1 the results of leaching tests of 5 different samples were presented. Each of the efficiency, E (%), represents the average from 5 results obtained for the samples of different granulation. In further experiments (results presented in Figs. 2–8) the influence of particle size was not tested and the leaching experiments were done with the whole sample, without grain-size analysis.

The results of experiments revealed that extraction of uranium was in the range of 64–81% (Table 3, entries 1–5). The other metals were recovered with the efficiency, as follows: V – 25–52%, Mo – 33–78%, Cu – 28–52%, La – 31–66%, Th – 67–80% (Fig. 1). The extraction of Zn and Ni was almost complete.

The impact of other factors, such as concentration of sulphuric acid and the contribution of calcination stage to the leaching efficiency, was also examined. The samples of dictyonemic shales with particle size in the range of 0–0.2 mm were treated with 48% or 95% sulphuric acid (“acid cure” method) for five or eighteen days. After this time, the samples were leached in the round-bottom glass flask with a reflux condenser connected (Star Fish™, Multi-experiment work station). The leaching experiments were performed also with non-calcinated samples by using 10% sulphuric acid. The comparison of the results of all experiments showed that the highest efficiency was obtained for samples, which were calcinated prior to the leaching and then

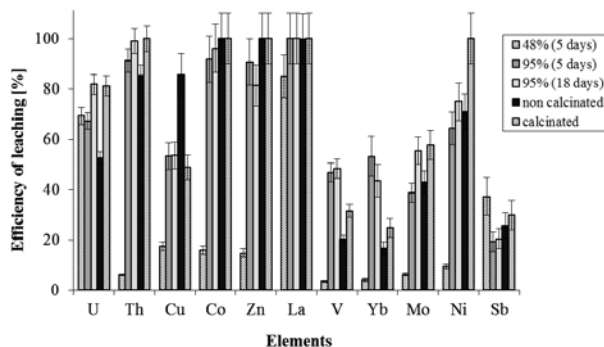


Fig. 2. Efficiency of acid leaching under different process conditions, dictyonemic shales (sample 21/10/8).

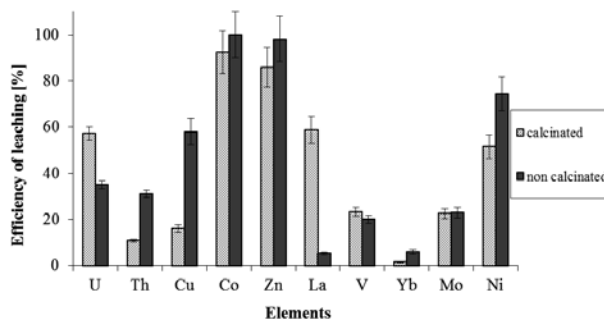


Fig. 3. Efficiency of acid leaching (10% H₂SO₄, 80°C, 8 h) of calcinated and non-calcinated samples of dictyonemic shales.

Table 3. The uranium leaching efficiencies from dictyonemic shales

| Entry | Sample notation | Calcination | Leaching solution ^{a)} | Oxidation agent | Temperature (°C) | Pressure (bar) | Time | Efficiency of leaching |
|-------|-----------------|-------------|---|------------------|------------------|----------------|----------------------|------------------------|
| 1 | 21/10/5 | + | 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 80 | 1 | 8 h | 72% ± 4 |
| 2 | 21/10/22 | + | 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 80 | 1 | 8 h | 81% ± 4 |
| 3 | 21/10/8 | + | 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 80 | 1 | 8 h | 64% ± 3 |
| 4 | 21/10/9 | + | 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 80 | 1 | 8 h | 68% ± 3 |
| 5 | 21/10/10 | + | 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 80 | 1 | 8 h | 78% ± 4 |
| 6 | 21/10/8 | - | 1) acid cure (48%) ^{b)} 2) 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 1) 25 2) 80 | 1 | 1) 5 days 2) 8 h | 69% ± 3 |
| 7 | 21/10/8 | - | 1) acid cure (95%) ^{b)} 2) 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 1) 25 2) 80 | 1 | 1) 5 days 2) 8 h | 67% ± 3 |
| 8 | 21/10/8 | - | 1) acid cure (95%) ^{b)} 2) 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 1) 25 2) 80 | 1 | 1) 18 days 2) 8 h | 82% ± 4 |
| 9 | 21/10/8 | - | 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 80 | 1 | 8 h | 35% ± 2 |
| 10 | 21/10/8 | + | 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 80 | 1 | 8 h | 57% ± 3 |
| 11 | 21/10/8 | - | 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 25 | 1 | 8 days | 51% ± 3 |
| 12 | 21/10/8 | + | 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 25 | 1 | 8 days | 55% ± 3 |
| 13 | 21/10/8 | + | 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 80 | 3 | 2 h | 60% ± 3 |
| 14 | 21/10/8 | + | 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 80 | 5 | 2 h | 64% ± 3 |
| 15 | 21/10/8 | + | 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 80 | 7 | 2 h | 59% ± 3 |
| 16 | 21/10/8 | - | 5% Na ₂ CO ₃ /5% NaHCO ₃ ^{a)} | MnO ₂ | 80 | 1 | 8 h | 30% ± 1 |
| 17 | 21/10/8 | + | 5% Na ₂ CO ₃ /5% NaHCO ₃ ^{a)} | MnO ₂ | 80 | 1 | 8 h | 42% ± 2 |

Further experimental details:

^{a)} 0.5 g of ground uranium ores and 0.01 g of MnO₂ (2% of total mass sample) were placed in a round bottom glass equipped with a back cooler, then 4 ml of H₂SO₄ or 2 ml of 5% NaHCO₃ and 2 ml 5% Na₂CO₃ were added.

^{b)} 2 g of ground uranium ores were treated with 48% or 95% H₂SO₄ for 5 or 18 days.

extracted with 10% sulphuric acid solutions, and for samples, which were leached by “acid cure” with 95% sulphuric acid (Fig. 2, Table 3, entries 6–8).

The analysis of experiments showed that uranium and lanthanum were leached with higher efficiency when the samples were first calcinated in the oven. Efficiencies of leaching uranium and lanthanum were 57 and 59%, respectively. In case of lanthanum very big difference between calcinated and non-calcinated samples was observed. The leaching efficiencies of V and Mo were at the same level. The prolongation of ore-acid contact time above 8 h did not result in significant increase of leaching efficiency (Figs. 3 and 4, Table 3, entries 9–12).

Leaching of the uranium ore was performed in the autoclave. The apparatus gave the possibility of adjustment of the parameters in a wide range, thus enabled to carry out the process optimization.

The acid leaching was carried out for 2 h, at 80°C under pressures: 3, 5 and 7 bar. The leaching parameters: temperature, quantity of sulphuric acid and

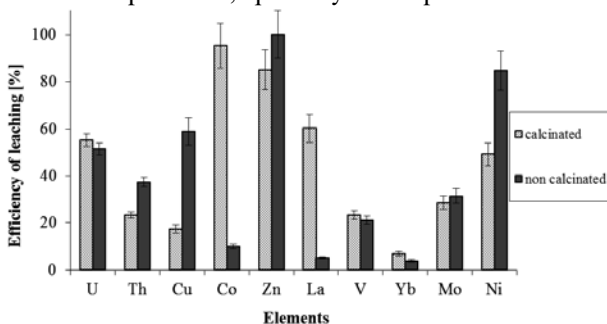


Fig. 4. Efficiency of acid leaching (10% H₂SO₄, 25°C, 8 days) of calcinated and non-calcinated samples of dictyonemic shales.

manganese oxide added, and the concentration of sulphuric acid, were adjusted on the basis of the results of previous experiments. In these conditions the recovery of uranium and other metals from the ores was in the range of 60–80%; only V and Cu were extracted with a 30% efficiency (Fig. 5). The influence of pressure in the experimental range was not significant. The leaching efficiency of uranium was in the range 59–64% (Table 3, entry 3, entries 13–15), molybdenum 56–60%, vanadium 29–32% and lanthanum 58–65%.

As in previous experiments, there was no influence of the particle size on leaching efficiency in 0–1 mm particle size range.

Leaching of dictyonemic shales with alkaline solution

Leaching of uranium and accompanying metals was performed with alkaline solutions of 5% Na₂CO₃/5% NaHCO₃, at 80°C for 8 h. The experiments showed that alkaline leaching was more selective than leaching

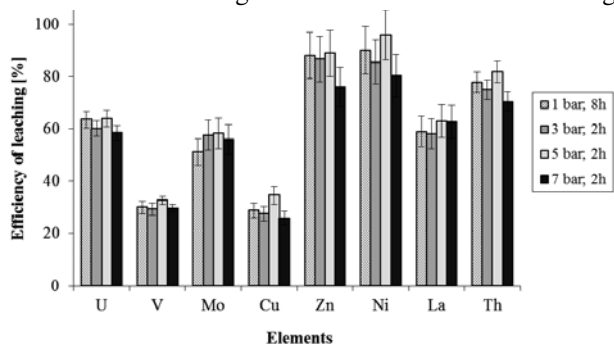


Fig. 5. Efficiency of acid leaching in the autoclave (dictyonemic shales, 10% H₂SO₄, 80°C, variable pressure).

Table 4. The uranium leaching efficiencies from sandstones under ambient pressure

| Entry | Sample notation | Calcination | Leaching solution | Oxidation agent | Temperature (°C) | Time | Efficiency of leaching |
|-------|-----------------|-------------|---|-------------------------------|------------------|--------|------------------------|
| 1 | 21/10/142 | – | 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 30 | 45 min | 40% ± 0.1 |
| 2 | 21/10/142 | – | 5% H ₂ SO ₄ ^{a)} | MnO ₂ | 80 | 45 min | 57% ± 4 |
| 3 | 21/10/142 | – | 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 80 | 45 min | 73% ± 2 |
| 4 | 21/10/142 | + | 10% H ₂ SO ₄ ^{a)} | MnO ₂ | 80 | 45 min | 47% ± 2 |
| 5 | 21/10/142 | – | 37% H ₂ SO ₄ ^{a)} | MnO ₂ | 80 | 45 min | 85% ± 0.2 |
| 6 | 21/10/142 | – | 5% Na ₂ CO ₃ /5% NaHCO ₃ ^{a)} | MnO ₂ | 80 | 45 min | 47% ± 2 |
| 7 | 21/10/142 | – | 5% Na ₂ CO ₃ /5% NaHCO ₃ ^{a)} | MnO ₂ | 80 | 8 h | 48% ± 2 |
| 8 | 21/10/142 | – | 5% Na ₂ CO ₃ /5% NaHCO ₃ ^{a)} | MnO ₂ | 22 | 7 days | 45% ± 2 |
| 9 | 21/10/142 | – | 8% NaOH/18% Na ₂ CO ₃ ^{b)} | H ₂ O ₂ | 80 | 45 min | 100% ± 5 |

Further experimental details:

^{a)} 0.5 g of ground uranium ores and 0.01 g of MnO₂ (2% of total mass sample) were placed in a round bottom glass equipped with a back cooler, then 4 ml of H₂SO₄ or 2 ml of 5% NaHCO₃ and 2 ml 5% Na₂CO₃ were added.

^{b)} 0.5 g of ground uranium ores MnO₂ were placed in a round bottom glass equipped with a back cooler, then 2 ml of 18% Na₂CO₃, and 2.5 ml of 8% NaOH were added followed by 0.5 ml of 30% H₂O₂ (1% of total mass sample).

with acid. In post-leaching solutions not all components of the ore samples, were detected; however, leaching efficiency of most of them was less than in the case of acidic leaching.

In the case of calcinated samples the uranium was extracted with 42% efficiency (Table 3, entry 17), molybdenum with 24% and vanadium with ca. 8% efficiency. For non-calcinated samples the efficiency of molybdenum leaching increased to 63% (Fig. 6). Very similar results for 8-day time of leaching at room temperature were obtained.

Leaching of sandstones with acidic solutions

The influence of such parameters as concentration of acid (5, 10 and 37% H₂SO₄) and temperature (30°C or 80°C) on uranium leaching from sandstones was tested. Preliminary experiments showed that the efficiency of leaching the metals from a calcinated sample was less (47%) than from a sample that was not pretreated in the oven (73%). The leaching tests were performed under ambient pressure with MnO₂ additive. It was concluded that acid concentration had the greatest influence on the extraction of uranium. The experiments performed with 10% H₂SO₄ lixiviant at 30°C showed the average efficiency of uranium extraction at a level of 40% (Table 4, entry 1). Other metals were extracted with the following efficiencies: Co – 69%, La – 25%, V – 1%, and Yb – 12%. Such metals as Th, Cu, V, and Ni were not detected in the post-leaching solutions. At

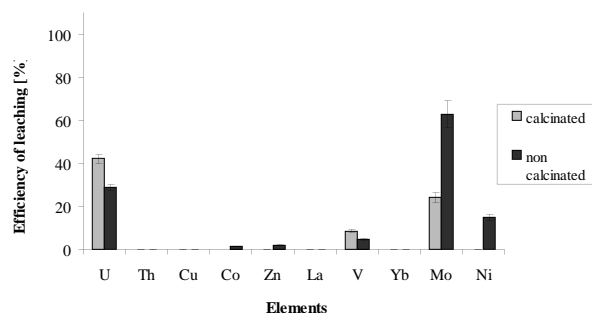


Fig. 6. Efficiency of alkaline leaching (5% Na₂CO₃/5% NaHCO₃, 80°C, 8 h) of calcinated and non-calcinated samples of dictyonemic shales.

higher temperature (80°C), the efficiency of uranium leaching increased to 73% (Table 4, entry 3); the other metals were extracted with the efficiency as follows: Th – 39%, Cu – 32%, Co – 74%, La – 41%, V – 45%, and Yb – 30%. The extraction of Ni was almost complete. The experiments proved that increase of acid concentration and increase of temperature resulted in the rise of uranium leaching efficiency (Table 4, entries 2–5 and 1). At a temperature of 80°C with a 37% H₂SO₄ lixiviant, the efficiency of uranium leaching reached 80%. The results are shown in Fig. 7.

Leaching of sandstones with alkaline solutions

The experiments were performed with 5% Na₂CO₃/5% NaHCO₃ as a leaching solution at a temperature of 80°C, with MnO₂ as an oxidizing agent. After 45 min of treating, the efficiency of uranium recovery was 47% (Table 4, entry 6) and the extension of time to 8 h did not considerably change this efficiency (Table 4, entry 7). The same results of extraction of uranium were observed after one-week treatment at room temperature (22°C) (Table 4, entry 8). It is important to notice that in the post-leaching solutions only uranium and vanadium were detected. The efficiency of leaching for U was 45% and for V – 25%.

Very interesting results were obtained when an 8% NaOH/18% Na₂CO₃ lixiviant was applied as a leaching solution with 30% H₂O₂ as an oxidizing agent (Table 4, entry 9). The almost complete extraction of U,

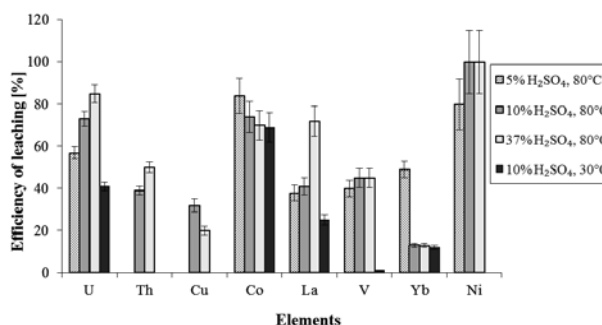


Fig. 7. Efficiency of acid leaching (various concentrations of H₂SO₄ and temperature) of sandstones.

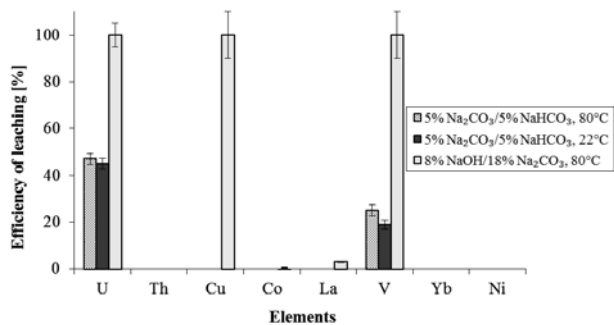


Fig. 8. Efficiency of alkaline leaching of sandstones.

Cu, V was observed in that case. The other metals, like Th, Yb, Co, Ni were not extracted from the sandstone ores. The leaching efficiencies of La and Mn were very low – 3 and 4%, respectively (Fig. 8).

ICP-MS method validation

To assure the accuracy of measurements the validation of all presented analytical procedures was carried out. Accuracy of the elaborated methods was demonstrated by analysing available CRMs. The uncertainty budget for elemental determination in standard reference material SOIL-5 was estimated. The expended uncertainty for coverage factor $k = 2$ (confidence limit 95%) has been evaluated to be 5–20%, depending on the determined element. For uranium, expended uncertainty was evaluated as 5%, because mass 238 is free from isobaric interferences, sensitivity for U is excellent, and the analytical blank was without uranium traces. For other elements, the expanded uncertainty was estimated as follows: Th – 5%, Cu – 10%, Co – 10%, Zn – 10%, La – 10%, V – 8%, Mo – 10%, Ni – 10%, Yb – 15%, Sb – 20%. The content of U, Th and other elements were in a good agreement with certified values (Table 5).

The uncertainty of the results of measurements generally consists of several components, which may be grouped into two categories according to the method used to estimate their numerical values: 1) those which are evaluated by statistical methods, 2) those which are estimated by other means. In our case, the total uncertainty was composed of uncertainties taken from

Table 5. Results of analysis of CRM: IAEA SL-1 (mg·kg⁻¹)

| Element | IAEA SL-1 Certificate | | INCT results by ICP-MS | |
|---------|-----------------------|---------------|------------------------|---------------|
| | U ($k = 2$) | | U ($k = 2$) | |
| Co | 19.8 | 18.3–21.3 | 18.4 | 17.3–20.1 |
| Cu* | 30 | 24–36 | 28.2 | 25.4–31.0 |
| Fe | 67 400 | 65 700–69 100 | 62 100 | 54 000–70 500 |
| La | 52.6 | 49.5–55.7 | 53.1 | 47.8–58.3 |
| Mn | 3 460 | 3 300–3 620 | 3 347 | 3 013–3 681 |
| Mo | n.d. | n.d. | 1.43 | 1.29–1.57 |
| Ni* | 44.9 | 36.9–53.9 | 42.7 | 38.5–46.9 |
| Sb* | 1.31 | 1.19–1.43 | 1.32 | 1.12–1.52 |
| Th | 14 | 13–15 | 13.9 | 13.2–14.6 |
| U* | 4.02 | 3.69–4.35 | 4.11 | 3.90–4.32 |
| V | 170 | 155–185 | 173 | 159–187 |
| Yb* | 3.42 | 2.77–4.07 | 3.14 | 2.67–3.61 |
| Zn | 223 | 213–233 | 212 | 190–234 |

* Information value n.d. – not determined in this material.

the analysis of CRM, recovery of standards, standard deviation (SD) from the repeatability and sample dilution. Estimation of uncertainty was carried out using type 1) method as well as method, 2) based on other than statistical approaches, such as the experience of the analyst and provided by the manufacturer specifications for instruments used. The major contributor to uncertainty of the analyses carried out in this work was dilution of samples and standards.

Conclusions

The samples of dictyonemic shales and sandstones from domestic resources were subjected to acidic and alkaline leaching to test the efficiency of uranium and accompanying metals extraction. The influence of such parameters as: temperature, pressure, particles size of solid material, the kind of leaching solutions (acidic or alkaline) and their concentration, was studied.

The results of experiments showed the method of sample preparation, before leaching tests, was a very important step in the process. In the case of the dictyonemic shales the calcination stage was necessary, but for sandstones the sufficient pretreatment procedure included only crushing the sample.

The best results of acid leaching of dictyonemic shales were found for treating them with 10% H₂SO₄ 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: V – 25–52%, Mo – 28–52%, Cu – 28–52%, La – 31–61% and Th – 67–80%. The extraction of Zn and Ni was almost complete. The same level of efficiency of uranium leaching was achieved after 2 h at 80°C and at 5 bar in an autoclave.

This experimental work showed that sandstones were more readily leachable in comparison with the dictyonemic shales. The leaching efficiency of uranium was in the range of 41–85% and depended on temperature and concentration of the leaching acid. All the metals accompanying uranium in the ores were present in post-leaching solutions.

The opposite effect was observed in the case of alkaline leaching process. It was found that uranium

can be selectively leached by alkaline solutions. In the case of 5% Na₂CO₃/5% NaHCO₃ lixiviants, only three metallic components of the ores were detected in the post-leaching solutions: U (42–63%), Mo (24%) and V (~ 8–25%).

It was found that uranium can be quantitatively leached by a mixture of sodium carbonate, sodium hydroxide and hydrogen peroxide. Apart from uranium, almost complete extraction of Cu and V was observed in that case. The selectivity of solid-liquid extraction stage can be important for process scheme design that will enable to separate not only uranium, but also some selected metals that are valuable and may be crucial for optimization of the process economy. According to the literature data, solid-liquid extraction of uranium from uranium ores higher than 90% is hardly to achieve. In the reported experiments applying acid leaching, 85% of efficiency was reached, which is not satisfactory. However, the results of alkaline leaching were more promising. The leaching efficiency obtained in the present work was even higher than that reported in the literature.

The solid-liquid extraction is a very important stage in the technology of uranium production from uranium ores. At this stage, it is important to extract as large as possible the amount of metals, which are of interest for the economy reasons. Appropriate selection of parameters such as temperature, pressure and process duration, as well as the quantity of reagents used, allows controlling the process efficiency. Apart from uranium, such components of the ores as molybdenum, vanadium or rare earth elements are considered for recovery. As was proved in the experiments, the leaching stage can be also selective to some components by appropriate selection of reagents. This gives some flexibility in process design and further arrangement of technological flowsheet. If one ever considers Polish low-grade uranium ores to produce the fuel for nuclear reactors, the recovery of other valuable metals probably will need to be considered in the technological scheme to improve economy of such a project.

The solid-liquid extraction is the first stage of the technology of uranium production that is followed by other steps: purification-concentration by ion exchange resins or liquid-liquid extraction/re-extraction and precipitation to obtain final product, yellow cake U₃O₈.

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