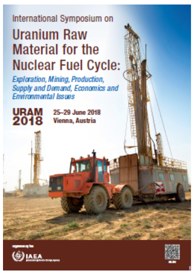

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Uranium from domestic resources in Poland

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INTRODUCTION

Uranium mining activities in Poland took place in Sudetes since the end of the 1940s until 1968. Industrial plants R-1 in Kowary carried out the processing of uranium ores till 1973. Outside Sudetes region, uranium was also found and mined from the Staszic pyrite deposit in Rudki, the Holy Cross Mountains. Total production of uranium in these times in Poland is estimated at about 650 t [1]. The mining activities resulted in remains of some 100 dumps, mostly abandoned, of waste rock and ore totalling approximately 1.4 x 106 m3 as well as one tailing pond, which has been the object of a remediation project partly funded by the European Commission aid in 2001 [2].

In the Polish Lowland, in the area of Podlasie Depression (NE Poland), concentrations of uranium were discovered in the Lower Ordovician Dictyonema shale. In the 70s of last century, there was found about 1400 tons of uranium at an average content of 250 ppm and 3800 tonnes of uranium of the ore content of 75 ppm ("Rajsk" deposit). Even then, this occurrence was considered as non-economic. The most interesting uranium mineralization on Polish territory occurs is in the Lower and Middle Triassic rocks of the central parts of Peribaltic Syneclise (N Poland). The highest concentrations were found in the sandstone-conglomerate continental series of Upper Bundsandstein, where for the layer of thickness of about 3.4 m, the average uranium content is 0.34%, with a maximum content exceeding 1.5%. Uranium is accompanied by other metals, like V, Mo, Pb and Se.

In January 2014 Polish Government adopted the Program of Polish Nuclear Energy [3]. One of the objectives of this Program is the assessment of domestic uranium deposits as a potential source of uranium for Polish nuclear reactors. The 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 global uranium market.

CONVENTIONAL RESOURCES OF URANIUM IN POLAND

Poland, like most countries in the world, has only the resources of low-grade uranium ores. In the period of 1948-1972, there were 5 mines extracting uranium ores. Four of them were located in the Sudetes, and only one outside of this region - in Rudki near Nowa Slupia, in the Holy Cross Mountains [1]. The uranium content in these deposits was typically about 2,000 ppm. Currently, no uranium mine is working in the country. In the second half of the 20th century, the Polish Geological Institute (PGI) made numerous assessments of prospects for exploration of uranium ore deposits in Poland [4]. According to the PGI estimates, the Ordovician Dictyonema shales of the Podlasie Depression (NE Poland) seem to be the most prospective, with uranium concentration in the 75-250 ppm range and the sandstones of Peribaltic Syneclise (Paslek-Krynica Morska), where uranium concentration reaches even 1, 5%. These deposits, as a potential source of uranium for Polish nuclear power plants, were investigated by the PGI and the Institute of Nuclear Chemistry and Technology (INCT) as part of the Operational Programme –Innovative Economy (POIG) project implemented in 2010-2013. Within the framework of the POIG project, Polish uranium deposits and their exploitation options were reassessed. Based on the archival ore samples from previously tested boreholes, various technological schemes and methods of obtaining uranium from Polish ores were examined with an initial economic assessment of the studied processes. Optimal leaching conditions for uranium from both Dictyonema shales and sandstones as well as uranium separation from other metals, like rare earth elements (REE) that have undergone leaching into the aqueous phase, have been found [5-8]. It has been shown that it is possible to sequentially separate these metals from the solution by means of ion exchange [9]. Uranium can also be separated using solvent extraction [10]. An alternative to solvent extraction carried out in traditional reactors or columns is extraction using membrane contactors, which constitute modern separation systems, allowing for two processes to be carried out: extraction and reextraction in one installation [11, 12]. An effective and selective extractant plays an important role in the extraction process. In recent years, great interest in new extracting agents of uranium like calixarene derivatives is shown [13]. The project developed a synthesis path for these compounds. They may also find other applications in the nuclear fuel cycle, e.g. for the separation of fission products and minor actinides from spent nuclear fuel. By using a membrane module with a helical flow in the uranium ore leaching process, high U leaching rates were obtained. In this system it is possible to simultaneously separate the leachate from the remaining solid phase (parent rock) [14]. Such a method of conducting the leaching process, with the simultaneous filtration of the sludge in the membrane contactor with the helical flow, became the basis for the patent application in the Patent Office of the Republic of Poland and the European Patent Office [15].

In 2014, Poland completed geological and technological analysis and modelling of the process of uranium extraction from low-grade Ordovician Dictyonema shale (black shale-type). Analysis has shown that the costs of obtaining raw material for production of 1 kg of uranium would be several times higher than the current market price of that metal [16].

URANIUM FROM UNCONVENTIONAL SOURCES

Although uranium concentrations in unconventional sources are low, all together they are inexhaustible sources of uranium for future use. One of these sources are phosphates, which constitute the raw material for the production of chemical fertilizers. These rocks contain the largest concentrations of uranium from all unconventional uranium deposits occurring in the world. In Poland, phosphorites are found in vicinity of Annopol, the Holy Cross Mountains. The exploitation of phosphate rock in the country began in the interwar period and was discontinued in the 1970s. The mine in Chalupki was closed in 1961, and in Annopol in 1971. At present, domestic demand for phosphate rock is entirely covered by import from countries such as Algeria, Senegal, Morocco, Egypt, Tunisia and Syria.

In the technology of phosphate fertilizers, the first stage is the production of phosphoric acid. In this process, ground phosphorites are treated with sulfuric acid, as a result of which phosphoric acid and insoluble calcium sulphate (gypsum) precipitate contaminated with the remaining raw material are obtained. Phosphogypsum after washing with water is directed to heaps as waste. Most of uranium contained in phosphorites goes to phosphoric acid. In Poland, in the 1980s at the Institute of Nuclear Chemistry and Technology and at the Wroclaw University of Technology, a technology for recovering uranium from phosphoric acid was developed for expected use in Chemical Works in Police. According to this technology, uranium can be extracted from phosphoric acid in a coupled extraction-re-extraction process. The mixtures of mono- and dinonylphenylphosphoric acids (NPPA) and D2EHPA and TOPO were used as extracting agents in this process.

In 2015, the Institute of Chemistry and Nuclear Technology together with PwC Sp. z o.o, as part of the Bridge Mentor project (NCBiR), prepared a preliminary analysis of the possibilities of obtaining uranium from industrial phosphoric acid by the hybrid method, which was a combination of solvent extraction with membrane processes. The project was presented at Chemical Works in Police (at present AZOTY Group).

Phosphogypsum usually contains many different components like heavy metals, among them also some amounts of uranium. During the production of phosphate fertilizers, part of the uranium contained in phosphate rock passes to solid waste and is collected in heaps. In Poland, phosphogypsum dumps are located in Police, Wizow and Wislinka near Gdansk. These landfills are heterogeneous in chemical terms, because over the years, various raw materials have been used for the production of phosphate fertilizers. In phosphogypsum samples from the landfill in Wislinka collected in 1997, uranium concentration was 4.03 ± 0.08 mg / kg, while in the samples from 2007 –only 0.65 ± 0.05 mg / kg [17,18]. The heap in Wizow, which is a residue from the production of fertilizers from apatites from the Kola Peninsula (magmatic rocks), does not contain uranium, but has a significant concentrations of REE. Uranium from phosphogypsum can be recovered by washing with sulfuric acid [19,20].

In some parts of the world there are carbon deposits with elevated uranium content. The average uranium concentration in Polish coal from mines located in the Upper Silesia, Lower Silesia and Lublin regions is approx. 2 ppm. Research conducted at the Polish Geological Institute did not show differences in content depending on the origin of coal [21]. Uranium can also be obtained from coal ash; its content in coal ash from Polish coal-fired power plants amounts to several ppm [22].

Another source of uranium can be the copper industry. Similarly, as in the Olympic Dam mine in Australia, uranium can be obtained as a by-product during the production of copper by KGHM. The studies of copper industry waste as an alternative source of uranium was conducted by INCT as part of the POIG project. The content of U in the tested waste samples was not high, while the occurrence of other valuable metals was observed [23]. The recovery of uranium and other metals from industrial waste, by-products and phosphates is currently being investigated by the INCT as part of a project coordinated by the International Atomic Energy

Agency.

Determination of uranium content in the fluids from hydraulic fracturing of shales in the process of searching for natural gas deposits, carried out in Poland, was performed at INCT. The highest U concentration found in the fluid samples was 3.5 ppm. The possibility of recovering uranium from these wastewater has been demonstrated [24].

The other possible secondary source of uranium can be uranium tailings and old dumps which were abandoned after exploitation of uranium mines in Sudetes. Reserves of uranium in waste heaps from prospecting and extractive operations in this region in the years 1948-1967 are estimated at 10 to 30 tU.

CONCLUSION

Research projects conducted in Poland in recent years have confirmed the presence of low-grade uranium deposits in Poland. Methods for its extraction from black shale and sandstones in the framework of the POIG project were developed. The results collected as part of the project confirmed that currently there is no economic justification for the exploitation of Polish ores with low uranium content, but the situation may change with the continuing development trend of nuclear energy in the world and gradual depletion of uranium resources in rich ores.

The secondary sources of uranium in the country were also assessed. The most promising ones are waste from the copper industry and phosphoric acid obtained in the production technology of phosphate fertilizers.

In May 2012, September 2013 and October 2013, three concessions for prospecting for polymetallic uranium deposit for a private company were granted (“Radoniow”, “Wambierzyce”and “Dziecmorowice”areas in southern region of Lower Silesia). At present, geological exploration of uranium ore is not conducted in Poland.

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