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## URANIUM POST-MINING WASTES AS A POTENTIAL RESERVE SOURCE OF URANIUM FOR NUCLEAR ENERGY PLANTS

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**Abstract:** Biotechnology is an effective and environmental friendly method of waste utilization and poor refractory ores exploitation, well known since 1949 and successfully developed in many countries: Spain, Bulgaria, USA, and Sweden. Biotechnology opens the possibility to obtain uranium as by-product in rare element recovery process (eg. Co, Au, Re, Rh, Pt) and positively affects the economic efficiency of technology. The research program of biological exploitation of waste and poor ores in Poland is presented. Microbial consortia able to oxidize iron under neutral and acidic conditions (Fe concentration in ore is 1.8–3.4%) are isolated and developed during project realization.

**Key words:** *uranium, bacteria, bioleaching, solid waste*

### Introduction

Uranium is commonly found in very small amounts in environment. All isotopes and compounds of U are toxic and radioactive. The average U concentration in the earth's crust is about 1.7–2.0 mg/kg (Kabata-Pendias and Mukherjee, 2007) and can be released to the surface and ground waters from rocks and ores by dissolution and desorption or by diffusion.

Soils of Poland contain average amounts of U at the value of 1.6 mg/kg (lowland) and up to >10 mg/kg in the mountain soils (Sudety Mts). Uranium is a basic fuel for nuclear power plants and U production was estimated at the level of 53.66 Gg (gigagrams) (ESA Annual Report 2010).

The uranium exploration and exploitation in the South-West Poland (Lower Silesia District) was carried out since 1925 when the first 9 Mg of uranium ore were mined of

which 690 mg of radium was extracted and mining was developing to 1962 and about 704 Mg of U was derived (Adamski, 2000). Nevertheless the old subsurface mines, piles and dumps are still involved in the geochemical cycle of the area. The dumping of mineral wastes containing 11 mining residues of radionuclides and heavy metals and their influence on the environment is a problem in many mining regions. Leaching of uranium and radionuclides is a serious environmental problem in many countries (Baranowski and Bozau, 2006; Kalinowski et al., 2004; 2006).

According to Piestrzynski et al. (1996) mined uranium ores explored in the Lower Silesia region were polymetallic and contained: pitchblende, uraninite, autunite, metautunite, uranocircite, torbernite, metatorbernite, uranophane, sklodowskite, gummite, fourmarierite and libegite. Investigations of the influence of mining activity on the natural environment revealed the local-scale radioactive contamination limited to the dumps and their nearest vicinity at four localities: Kowary-Podgorze, Radoniów, Kopaniec and Kletno. It is worth mentioning that some fragments of uranium ores contain up to 0.15 wt.% of U in the dump material. However, the content of uranium deposited in piles and dumps remains completely unrecognized although it may be a source of this element recovered by biotechnology.

Exploitation of refractory ores and uranium post-mining wastes in Poland is considered as reserve source of uranium for nuclear power plants. The Frame Program of Activities for Nuclear Energy predicts the recognition of different way of uranium source exploitation including the use of biotechnology. Uranium ores in Poland contain approximately 250 to 1100 mg/kg U and the total hypothetical amount of uranium in Poland was estimated at 0.1 Gg. Average demand of uranium for 1 GW energy is calculated at the level 180 Mg and it was estimated that projected Polish nuclear plants need about 32.4 Gg uranium during sixty years of exploitation (Miecznik et al., 2011)

Upper Carboniferous and Lower Permian rocks (Grzmiąca, Wambierzyce and Okrzeszyn deposits) and origin of sandstone type uranium deposits are located in the Lower Zechstein mineralization in Fore-Sudetic Monocline, Poland and in the Region of Wałbrzych and Jelenia Góra. The studies revealed that in the Lower Zechstein mineralization the chief carriers of radioactive elements (U and Th) are organic compounds occurring in shale (Kupferschiefer) and shale in Zechstein sandstone conglomerate, and that thorium appears only in trace amounts. Maximum U contents in shale are 163 ppm. The only exceptions are samples with large secretion-type concentrations of thucholite. In one of them the U content was as high as 0.89%. Average uranium concentration in Grzmiąca deposit is 540 mg/kg and the total uranium content is calculated at the level of 670–820 Mg and in Okrzeszyn deposit about 937 Mg (Solecki et al., 2011). Uranium content in other sandstone type deposits was calculated at the level of 1.1 Gg.

Preliminary studies carried out in the first stage of project “Meeting the Polish nuclear power engineering’s demand for fuel – fundamental aspects” which is realized in the frame of strategic research program “Technologies Supporting Development of Safe Nuclear Power Engineering” were focused on sampling of refractory ores and

uranium post-mining wastes deposited in dumps and piles in Lower Silesia region. The concentration of U and Th, Cu, Co, Mn, Zn, La, Yb, Mo, Ni, Sb and Fe was estimated using ICP-MS technique after acid digestion of mineral sample in high pressure microwave digestion system or alkali fusion. Results received for uranium and iron from the richest dumps are presented in Table 1.

Table 1. Uranium concentration, pH and dose rate in materials deposited in selected piles of Kłodzko and Jelenia Góra Valleys

No.	Sample	pH	$\mu\text{S/h}$	Background $\mu\text{S/h}$	U mg/kg	Fe mg/kg
1.	Grzmiąca	4.2–5.8	0.51–1.94	0.14	20.5–112,8	23978–35556
2.	Okrzeşzyn	6.1	2,5	0.22	86,3–130	20300–3600
3.	Kletno	5.8–7.0	0.20–0.61	0.22	4.82–62.3	46000
4.	Bobrowniki	5.2	1	0.22	143	58500
5.	Dziećmorowice	6.9	0.77	0.22	195	26900
6.	Radoniów	5.8–6.0	1.5–4.4	0.22	306–801	18700–25200
7.	Kromnów	5.7	4.2–16.8	0.22	2261	20200
8.	Kopaniec	6.1	2.8	0.22	733–2400	65800
9.	Wojcieszyce	4.6	1.7	0.22	193	27800

These preliminary results clearly show that material deposited in dumps may be useful for bioleaching (biotechnological) processes.

Biotechnology is an effective and environmental friendly method of waste utilization and poor refractory ores exploitation, well known since 1949 and successfully developed in many countries: Spain, Bulgaria, USA and Sweden. Biotechnology opens the possibility to obtain uranium as by-product in rare element recovery process (eg. Co, Au, Re, Rh, Pt) and positively affects the economic efficiency of technology (Chmielewski et al., 2002).

The known industrial applications of uranium ores/waste bioleaching are based on chemical-bacterial leaching, percolation leaching, mine waters biotransformation and heap/dump leaching. Bioleaching technique could be and practically is economic on an industrial scale when using materials containing below 0.03%  $\text{U}_3\text{O}_8$ .

Bacterial leaching of uranium is a two-step process (Figs 1 and 2). First, pyrite bioleaching is carried out, then the product of this process leaches the uranium ore/material. All applied industrial technologies are carried out in acidic environment but bioleaching processes on large laboratory scale in neutral or slightly alkaline pH were described. The main microorganisms used in these processes belong to the genus *Acidithiobacillus*, *Leptospirillum* and *Sulfobacillus*. Other microorganisms including

heterotrophs, fungi (e.g. *Penicillium* sp.) and yeasts (e.g. *Rhodotorula* sp.) are useful in this process. All mentioned microorganisms show high tolerance to heavy metals ions as well as uranyl ions (Munioz et al., 1995; Chmielewski et al., 2002).

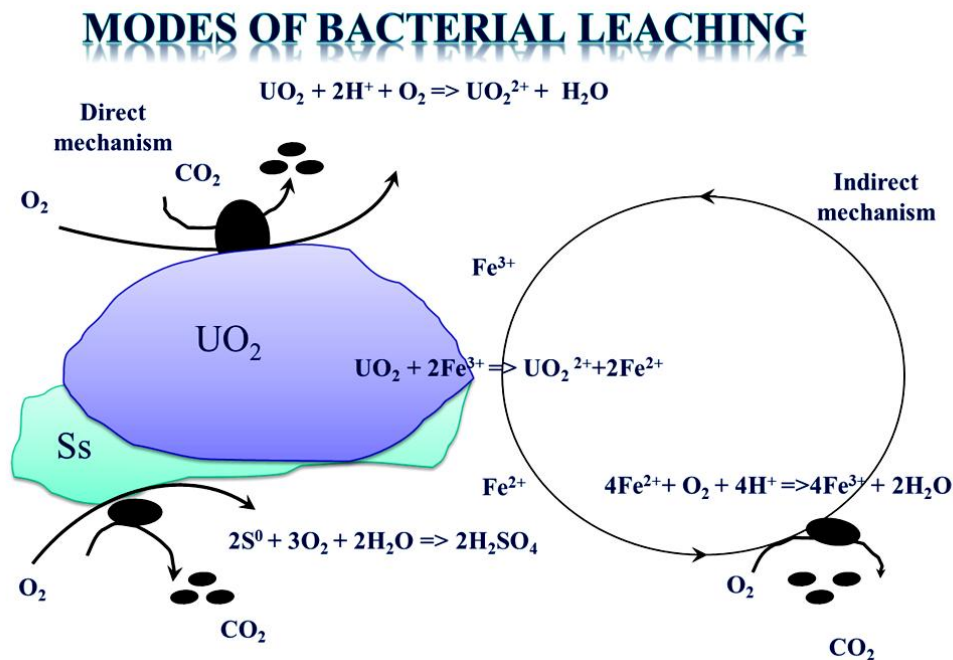


Fig. 1. Direct and indirect bacterial leaching of uranium

The efficiency of bacterial bioleaching processes can reach 98% of metal content. Some species of fungi are able to leach uranium in indirect way (Fig. 1). This process was described by Mishra et al. (2009) for the ore of Jaduguda, Bhatin and Nawapahar of UCIL India. The strains isolated from mine water were used for *in situ* leaching of mainly oxide low grade uranium ore of Turamdih mine containing 0.03%  $U_3O_8$ . The maximum recovery of 71% uranium was obtained with the strain *Cladosporium oxysporum*. The other two strains belonging to *Aspergillus flavus* and *Curvularia clavata* gave 59% and 50% of metal recovery, respectively, from the same ore.

We have isolated and developed 25 microbial consortia able to oxidize iron under neutral and acidic conditions (Fe concentration in ore is 1.8–3.4%) during realization of the mentioned strategic project. Microbial consortia active in neutral pH were able to acidification of culture. The 8 most active consortia were chosen for further experiments and they were able to acidify the environment from pH =7.0 to < 3.0 in 14 days.

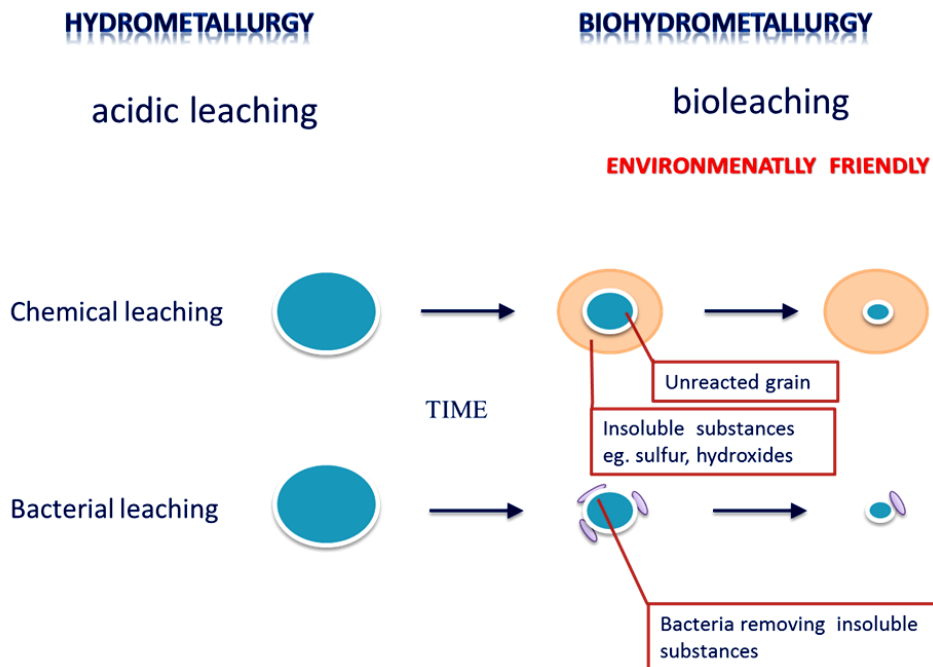


Fig. 2. Comparison of chemical and bacterial leaching process

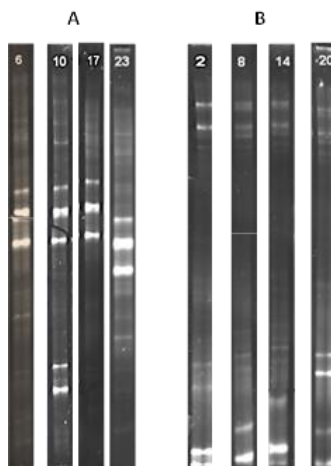


Fig. 3. The 8 most active consortia after Denaturing Gradient Gel Electrophoresis (DGGE). **A** – Microbial consortia active in neutral pH were able to acidification of culture and acidify ore/waste suspension from pH=7.0 to < 3.0 in 14 days. **B** – Consortia able to grow in acidic condition in pH 1.5–2.5

The most active consortia in both acidic and neutral pH were isolated from the Kromnów dump which contains the richest uranium material (up to 2261 mg/kg, Ta-

ble 1). Three unidentified species can be distinguished in microbial consortia active in neutral pH and 4–6 species in consortia growing in acidic conditions (Fig. 3).

Bioreaching efficiency reached during preliminary experiments was:

- in neutral pH – up to 30% of uranium content in ore/waste,
- in acidic conditions without any amendments 90%

and efficiency of chemical leaching with sulphuric acid was 10–60% of uranium content in ore/waste without bacteria.

## Conclusions

The presented results are preliminary and they were received during the first 4 months of project realization. However, they seem to be very promising for biotechnological application. The biometallurgy technique has to be considered for some low small and specific grade sources because of its efficiency and low environmental impact if it is used cautiously under well described environmental condition. Moreover, this technique may be used for environment reclamation in post-mining areas. The economic efficiency may be significantly improved by the recovery of rare metals present in wastes and ores. The economic risk of development of new biotechnology of microbial leaching of the substrate for nuclear fuel production is lowered by the alternative use of recovered uranium for production of  $UO_2/UO_3$  catalyst based on nanoparticles produced by microorganisms under anaerobic conditions.

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