

Deposits of Uranium in Serbia and possibility of “In-situ” Leaching

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Abstract

In Serbia there are many uranium ore bodies for which possibilities of exploiting by in situ leach method were conducted. Below we are giving the basic data concerning some ore bodies. Mountain “Stara Planina” is a unique mountainous massif, located on a territories of Serbia and Bulgaria. It belongs to the Carpatho – Balkan arc, which from Rumania, through Eastern Serbia extends to Bulgaria. In geostructural composition of Eastern Serbia, “Stara Planina” is within a “Stara Planina” structural formative zone, which is positioned between the Moesia platform on the east, and a Kucaj-Homolje structural-formative zone in the west. Massif of “Stara Planina” consist of three geotectonic enteties: Vrska Cuka anticline with Minicevo-Kadibogaz syncline, anticlinorium of “Stara Planina” and North-West parts of Knjazevac’s syncline. “Stara Planina” as a whole represents a distinct metallogenetic district within a Porec-Stara Planina metallogenetic zone. Deposits and occurrences of uranium are, at the moment, present only within an anticlinorium of “Stara Planina”.

Exploitation of Uranium ore can be performed in situ leaching or in heap leaching on the open pit or mine pit. In the process of “In-situ” leaching leaching solution is pumped into the deposit, where it makes contact with the ore. The solution bearing the liquefied ore content is then pumped to the layer and processed. This process permits the extraction of metals and salts from an ore body without the requirement for conventional mining, entailing drill-and-blast, open-cut or underground mining. “In-situ” leach (ISL) mining is defined as the extraction of uranium from the host sandstone biochemical solutions and the recovery of uranium at the surface. ISL extraction is conducted by injecting a suitable leach solution into the ore zone below the water table; oxidizing, complexing, and mobilizing the uranium; recovering the pregnant solutions through production wells; and, finally, pumping the uranium bearing solution to the surface for further processing. Acid leach technology employs an acid based leaching system. Dilute sulfuric acid is normally used.

Introduction

The element uranium is very widely distributed throughout the crust of earth. Almost all types of rocks contain some amount of uranium. Acid igneous rocks, like granites, syenites etc., are rich in uranium, whereas basic and ultrabasic rocks are depleted of uranium. Uranium is also present in river water, ground water and even in seawater. But, the common source of uranium for mankind are the rocks, uranium ores have a low content of uranium. The rich uranium deposits are very rare on earth. Uranium is commonly understood as a material which has a huge energy and its only commercial application is as nuclear fuel. But apart from its use in nuclear power plants, the possibility of its use in nuclear weapons makes the material of strategic importance and, thereby, restricts its free global trade.

“In-situ” leach (ISL), also known as “In-situ” recovery (ISR), uranium mining technology was developed independently in both the USA and USSR in the early 1960s. The method was conceived for extracting uranium from infiltration sandstone type deposits located in water saturated permeable rocks that were not suitable for conventional mining. It was developed in both countries using similar engineering and technological approaches. However, the Soviets adopted the acid leach system, while the US specialists employed an alkaline, primarily carbonate based system. In following years the acid ISL technology was also applied in Bulgaria, Czechoslovakia, the German Democratic Republic and China. By 1998 and 1999 new acid leach projects were being developed in Australia.

Chemically, metallic uranium is highly reactive. The properties of uranium, particularly its solubility, ease of transport and precipitation, have led to the formation of ore deposits of a number of types in a variety of geological settings. These deposits can be formed at the surface, at low temperature in recent environments or in deep seated older formations.

Leaching of uranium and other potentially valuable associated components can be done with acid or carbonate reactants. These include sulfuric, nitric and hydrochloric acids, sodium carbonate and bicarbonate, ammonium carbonate and bicarbonate, as well as potassium carbonate compounds, in acidic or alkaline

environment. Based on a comparison of experience between conventional and ISL uranium mining, ISL mining was found to have the following advantages:

- low capital and operational project costs;
- high cash flow within one year;
- rapid payback of investment;
- reduced length of project development and startup;
- low power consumption and less equipment required.

Part I: Deposits of Uranium in Serbia

In Serbia there are many uranium ore bodies for which possibilities of exploiting by “In-situ” leach method were conducted. Below we are giving the basic data concerning some ore bodies.

“Stara Planina” is a unique mountainous massif, located on the territories of Serbia and Bulgaria. It belongs to the Carpatho – Balkan arc, which from Rumania, through Eastern Serbia extends to Bulgaria (Fig.1).

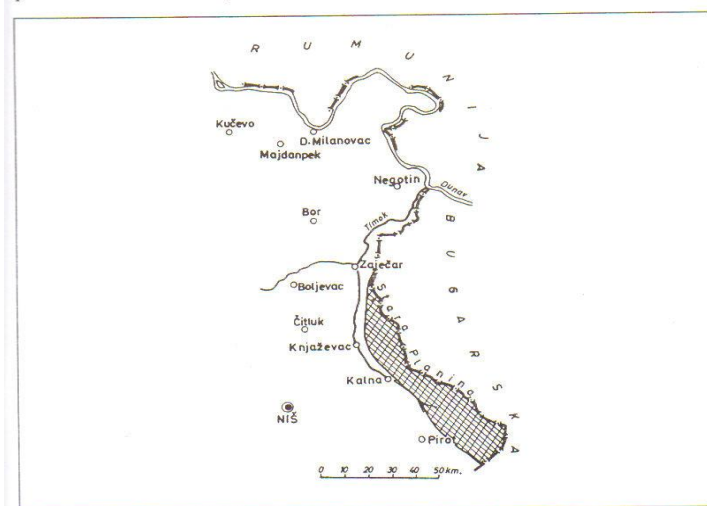


Fig. 1: Position of “Stara Planina” masif

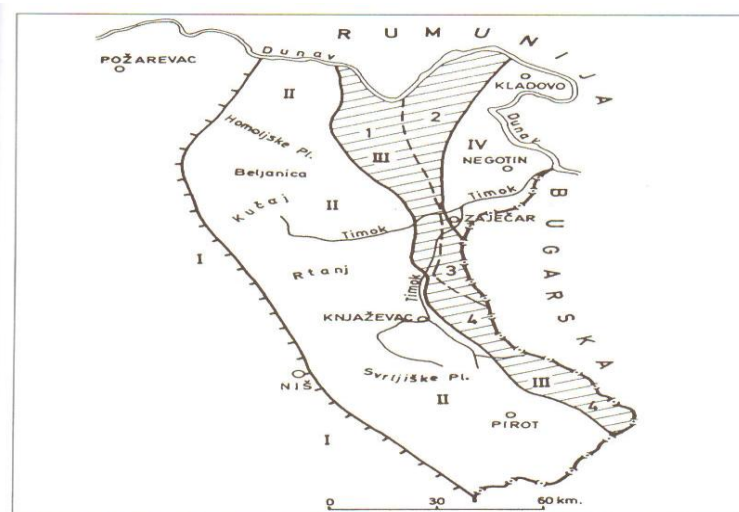


Fig. 2: Position of Porec “Stara Planina” zone within Carpatho-Balkans of Eastern Serbia

In geostructural composition of Eastern Serbia, "Stara Planina" is within a "Stara Planina" structural formative zone, which is positioned between a Mezijska platform on the east, and a Kucaj-Homolje structural-formative zone in the west (Fig. 2). Massif of "Stara Planina" consists of three geotectonic entities: Vrska Cuka anticline with Minicevo-Kadibogaz syncline, anticlinorium of "Stara Planina" and N.W. parts of Knjazevac's syncline. "Stara Planina" as a whole represents a distinct metallogenetic district within a Porec-Stara Planina metallogenetic zone. Deposits and occurrences of uranium are, at the moment, present only within an anticlinorium of "Stara Planina".

Bearing in mind known experiences from evaluation of potentiality of uranium resources, in this publication we devote greater attention to lithostratigraphic articulation, since it is, in contrast to chronostratigraphic, defined according to physical properties of the rocks, irrespective of biostratigraphic borders, that is of biological content, from the aspect of media favorable for formation of uranium deposits. Geological composition of "Stara Planina" includes gneisses and amphibolites, igneous complexes, diabase-phyllite formation, volcanic and volcanic-sedimentary products, complex of clastites and sediments of middle Triassic, Jurassic and Cretaceous age.

Into gneisses and amphibolites during the Caledonian orogeny, gabbros (Zaglavac's massif), granitoid rocks (Suvodol's and Radicevo's massif) and gabbro-granitoid complex of Janja were intruded. Diabase-phyllite formation is represented by sericite schists, marble, green rocks and green schists. In the upper part of diabase-phyllite formation from the molasse sediments and products of volcanism, metaconglomerates, metasandstones and schists of Inovska series were formed. During the Hercynian orogeny granites of Ravno Bucje were intruded and volcanic products were formed in a shape of smaller intrusions (granodiorite porphyrite) at Aldinac and Repusnica, numerous dikes and veins of quartz porphyres, as well as porphyrite pyroclastites.

Complex of clastites of "Stara Planina" spreads on the area of about 200 square km. with thickness of about 1.800 m. That is a formation with clearly defined continental sedimentation. Within this formation there are three separated members: lower member "Topli Do", of thickness of up to 100 m. (basal conglomerates, red sandstones, siltstones, clay stones), middle member "Kopren" of thickness of 250-500 m. (pale red quartz conglomerates, red coarse grained sandstones) and upper member "Dojkinci" of thickness of 150-300 m. (mottled series). Member "Dojkinci" or, mottled series, gradually upwards turns into marls, sandy limestones, dolomite limestones and limestones of middle Triassic age. Rocks of Jurassic age are represented by Estruska facies with coal, sandstone, limestone, conglomerate and schist facies. Rocks of lower Cretaceous age are represented by sandy limestones and marls. Sediments of upper Cretaceous age are developed within a limestone reef facies. Along the N.W. rim of "Stara Planina" Tertiary sediments occur, represented by sands, clays, conglomerates and marls with coal of Neogene age.

All rock masses of "Stara Planina" were tectonically "dealt with" during all of the orogeny cycles, when particularly were damaged middle and northern parts of anticlinorium of "Stara Planina". Metallogenetic district of "Stara Planina" consists of deposits and occurrences of uranium, occurrences of copper and molybdenum (Aldinac-Repusnica), polymetallic mineralization in the regions of Vratnica-Mali Izvor and Radicevac-Novo Korito, deposit of bismuth and copper Aljin Do, Au-Ag-polymetallic occurrence near Srebrena Glava, occurrences of Cu mineralization near Topli Do and deposits and occurrences of iron in the region of Jurassic products of Vidlicka zone.

According to the conditions of genesis and mineral paragenesis in the region of "Stara Planina" we separate: mineralization of uranium in the pegmatites near the village Radicevac, where is along one long fracture located known mineralogical occurrence of uraninite, high temperature uranium mineralization of hydrothermal district near Aldina Reka, Gornji Krst, Aldinac and Repusnica, hydrothermal deposits and occurrences of uranium in the lower part of the mottled series and infiltration occurrences of uranium in the sediments of Neogene age, metamorphic occurrences of uranium in the Inovska series.

According to the spatial location and geological media in which deposits and occurrences of uranium of "Stara Planina" are located, we distinguish five ore fields: magmatic-metamorphic complex of Janja, Aldinac-Repusnica, Inovska series, mottled series and Tertiary sediments. Ore field, magmatic-metamorphic complex of Janja, consists of amphibole gneisses and amphibolites, metamorphosed gabbros, granites (which occupy the largest area, about 30 square km.), contact alcalic-metasomatic products (syenite-diorite), serpentinite, and vein products (diabases, pegmatites and aplites). (Fig.3.).

Within this ore field there are occurrences of uranium and thorium as a result of high temperature mineralizations of hydrothermal district near Aldina Reka and Gornji Krst, as well as hydrothermal deposits (Mezdraga and Gabrovica) and occurrences (Srnci Do, Oraski Do, Javorski Do and other) of uranium. Occurrences of uranium and thorium near Aldina Reka and Gornji Krst are connected to a zone of contact metamorphism of granites and serpentinites. Here we distinguish between uranium-thorianite and allanite mineralization in the region of Aldina Reka and allanite mineralization near Gornji Krst. Uranium-thorianite mineralization occurs as zones in

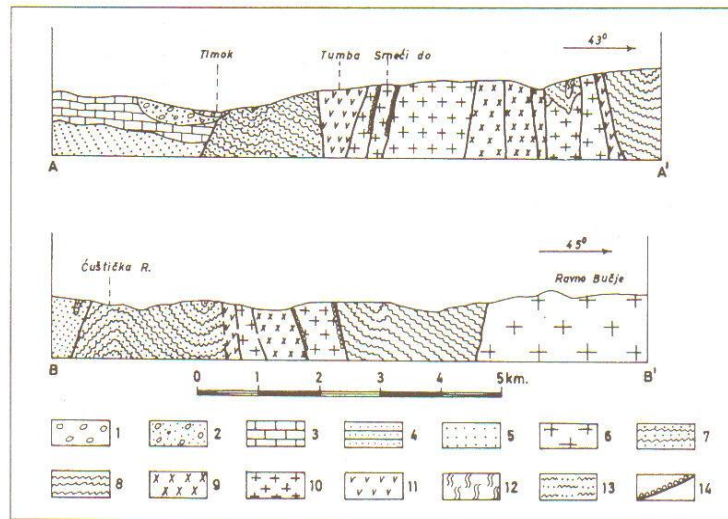


Fig. 3: Geological profile of granite bulk Janja and it's brin.

1-Alluvium; 2-Sands and clays; 3-Massive limestone; 4-Grey sandstone and conglomerates;
6- Granite of Ravno Bucje; 7-Inovska series; 8-Diabase-phyllite formation; 9-Alkaline metasomatic altered rocks; 10-Granite of Janja; 11-Gabbro rocks; 12- Serpentinite; 13- amphibole gneiss and amphibolite; 14-Mineralized.

serpentinite or at a contact of granites and serpentinites and allanite mineralizations occur as nests or accumulations in crushed zones at a contact of granites and serpentinites.

Hydrothermal veinlenticular deposits and occurrences of uranium of magmatic-metamorphic complex of Janja are connected to a big deep faults, which were formed during and after main phases of ground consolidation, and were reactivated later on a several occasions, which can sometimes be observed in a multistage felling of mineralized spaces. Formation of these deposits and occurrences was enabled by following prerequisites: relatively high average content of uranium in granites of Janja (fig. 4, 5, 6). Presence of minerals that can be a source of uranium, high percentage of soluble uranium, markedly dense network of faults, fractures and fissures, presence of geochemical barriers in a favorable structural conditions for deposition of uranium from solutions, and in a final formation of deposits and occurrences, considerable part was played by erosion level of the complex with a regime of underground waters, that has a great depth of circulation. Because of these conditions in a domain of deep faults depending on an erosion level, redistribution of uranium takes place in a sense of its content in lower parts, and in some cases depending on a regime of underground waters, presettlement of uranium into upper parts closer to surface, takes place.

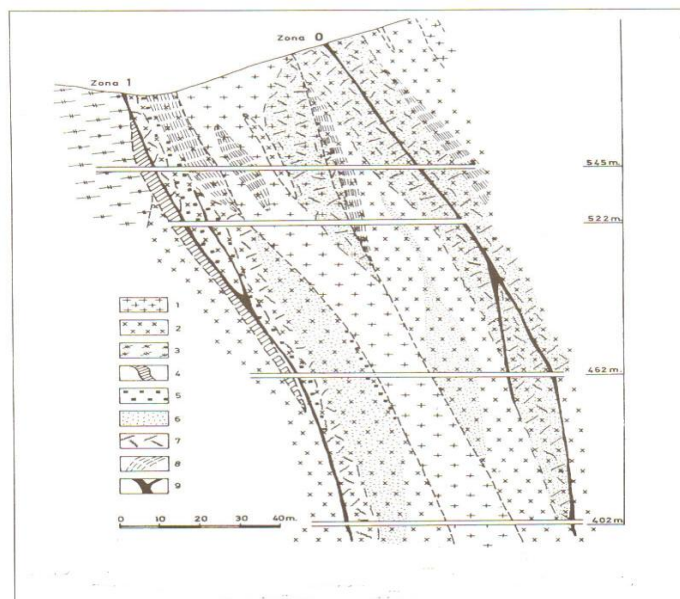


Fig. 4: Geological profile of "Mezdraja"

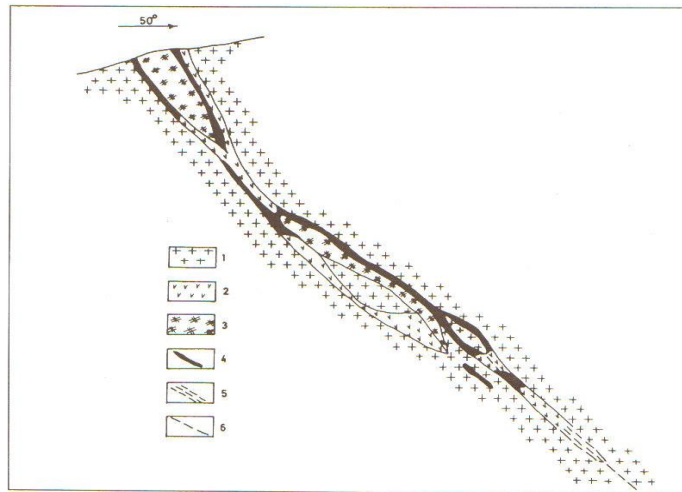


Fig. 5. Schematic transversal profile of fault zone 1 of "Gabrovica" deposit (MrS. S.Gertik, 1976)
 1- Granite; 2- Parts of the diabase dike; 3- Lenses of quartz;
 4- Mineralized intervals of altered diabase and granite;
 5- Clayey fault zone; 6- Clayey fracture

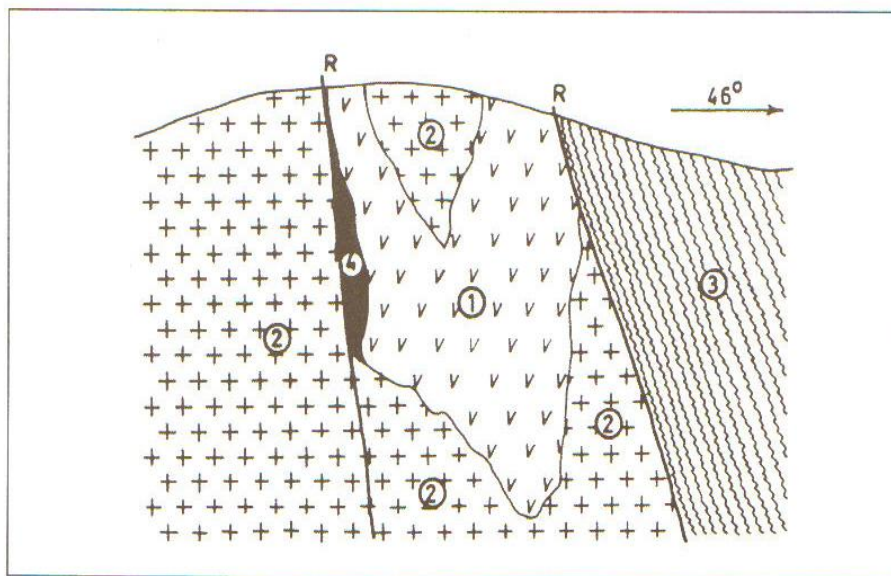


Fig. 6: Schematic profile of occurrence Srneci Do (Getik, 1991)
 1-Metamorphosed gabbro rocks; 2-Granite; 3-Phyllites; 4-Ore body

In a deposit Gabrovica (fig. 7), whose main ore mass is located in a subsurface parts, we have a typical example of redistribution of uranium from lower into an upper parts of a zone, with very little, almost none of the hydrothermal changes, and abnormal distribution of radioactive balance, that is in deeper parts of a zone disturbed in favor of radium.

In a deposit Mezdraja (fig. 8), main ore mass is located on an almost same absolute height as an ore mass in Gabrovica, only here being completely preserved on a depths of 100-150 m. below surface, as a typical hydrothermal mineralization with an entirely normal distribution of values radioactive balance, that is without any disturbances what so ever.

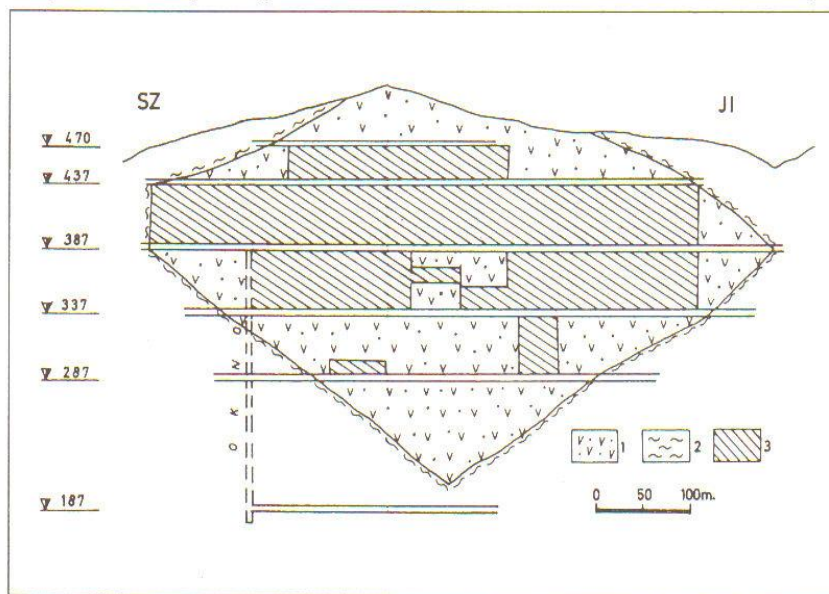


Fig. 7: Mineralized zone of deposit Gabrovica

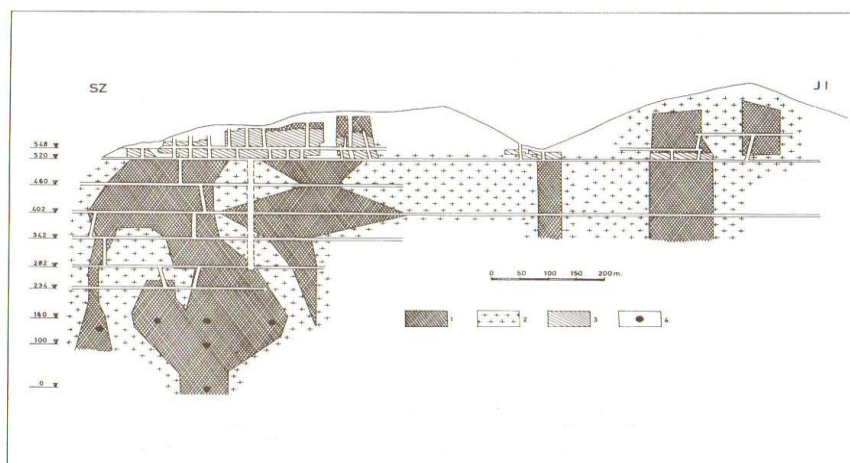


Fig.8: Mineralized intervals (1) along the strike of fault zone “0” of “Mezdraja” deposit;
2-Non-mineralized intervals; 3- Excavated intervals; 4-Completed boreholes (Gertik1986)

Deposit Mezdraja is located in a S.E. part of magmatic complex of Janja, and consists of fault zones “0” and “1” of general strike N.W.- S.E. with a deep towards N.E. Fault zone “0” was explored along the strike for 1.300 m and along the height from 200 m. to about 600 m. Zone “1” was explored along the strike about 400 m and along the height from 250 m to 300 m. Along the height in zones, zonal composition is observed. Besides always present crushed granites, which are cemented by siliceous and carbonate cohesive in upper levels, kaolinized, sericitized and chloritized parts are predominant while in a deeper parts silification, pyritization and hematization are more noticeable. Primary aureoles of dispersion of soluble uranium indicate link between uranium mineralization and fault zones and indicate that the most favorable places for uranium deposition are defined by the change of a dip angle and branching of structures ore minerals are pitchblende and secondary pitchblende, and they occur as dispersed impregnations, thin veins, nests, films, coats (fig. 9).

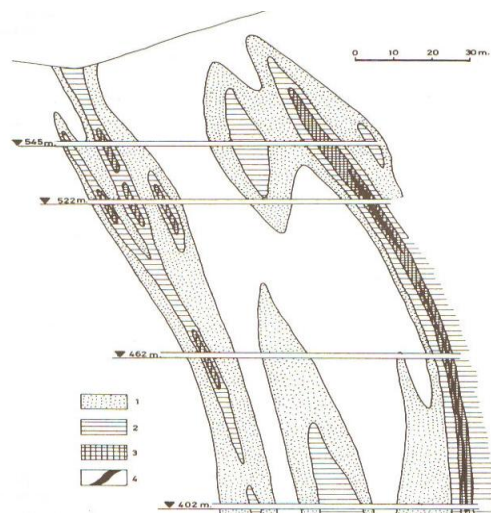


Fig. 9: Geological profile of "Mezdereja" deposit (Cukucan, 1965),
Content of soluble uranium: 1. 25-50 ppm; 2. 50-100 ppm; 3. 100-150 ppm; 4. 150-300 ppm

Deposit Gabrovica is located in N.W. part of southern belt of granites, of magmatic-metamorphic complex of Janja and consists of 8 fault zones. Fault zones 1, 3 and 3a consist of more or less altered and tectonically damaged diabase dikes, crushed granites and lenses of milky white quartz. Fault zones 2, 3, 4, 5 and 6 are filled with crushed granite, but the level of exploration being at a very low level. To the most detail was explored zone 1 which extends in N.W.-S.E. direction and has a dip towards N.E., dip angles varying from 20 to 80 degrees. All other zones are generally parallel to the zone 1.

Fault zone 1 was explored along the strike up to 600 m, and along a dip about 180 m. Diabase dikes were mainly transformed into hornblende, and along strike and dip framed by fractures filled with clay. Higher concentrations of uranium are mainly connected to wet portions of chloritized phyllonite and crushed granite, which are usually also soft. Dry and hard portions of these rocks are either entirely sterile or very weakly mineralized. Lenses of quartz are completely sterile. Kaolinitization, sericitization and chloritization are generally present in this deposit. Hematitization is very rare. Silicification doesn't exist at all.

Besides deposits Mezdereja and Gabrovica, in granites were observed about ten occurrences of uranium connected to fault zones of similar characteristics as fault zones of deposit Mezdereja. The most interesting are occurrences Srnci Do and Oraski Do. Occurrence Srnci Do is located in a middle part of main mass of granites of Janja which is characterized by a row of fault zones. The most striking fault zone, wide about 27 m., controls mineralized lenses in the zone itself and in hanging wall.

Occurrence Oraski Do is connected to a contact of granites and lenses of metamorphosed basic rock, granite at a contact being enriched by colored components and schistose. Mineralization occurs in a shape of thin veins and smaller lenses of clearly noticeable pitchblende. Ore field Aldinac-Repusnica consist of intrusions of granodioriteporphyrites, porphyrites, quartzporphyres and quartz-porphyrites in gabbros of Zaglavski massif and rock of diabase-phyllite formation. In this ore field are observed: chalcopyrite-uraninite veins, molybdenum-uranium impregnation and uranium bearing veins in crushed granites with pyrite and galena. Besides these, on a broader area of spreading of diabase-phyllite formation, numerous dikes and veins of graniteporphyres, quartzporphyres, granodioriteporphyrites and quartzporphyrites were identified, which indicate favorable structures for formation of uranium deposits.

Ore field "Inovska series" lies transgressively over metamorphosed gabbro rocks of S.W. brim of magmatic-metamorphic complex of Janja, and is being composed of metamorphosed conglomerates and arcose sandstones with graphite schists phyllites, argillophyllites and argilloschists. Metaconglomerates and sandstones are pierced by albitised microdiorites. Metamorphic occurrences of uranium "Ivovska reka" and "Tumba" connected to metasediments were formed as a result of a redistribution and preconcentration of uranium under the influence and conditions of dynamothermal metamorphism in a favorable structural-lithological media. There are strong indications that within metasediments are located metamorphosed and cataclastic quartzporphyres or their pyroclastic equivalents.

Ore field “Mottled series” or member “Dokinci” represent final part of clastite formation of “Stara Planina” whose most productive part is located in a region “Dojkinci-Jelovica-Rosomaca”. In this part of the ground, over crystalline base which consists of diabasephyllite formation, lie typical continental products, formed by the action of streams and torrents, primarily fragments of surrounding crystalline schists and granites, which belong to the member “Kopren”. Concordantly over member “Kopren” lies mottled series which was formed during the phase of subsidence and of approaching of the edge of deeper water basin on the mild slopes of nearby granite-crystalline elevations. In the hanging wall of the mottled series are marls and sandy stones of middle Triassic age. Generally this series has a strike N.W.-S.E. and a dip angle from 5 to 30 degrees, most frequently about 12 degrees. Mottled series consists of greyish-greenish-reddish fine grained, rarely medium grained sandstones, red medium grained up to fine grained and silty sandstones, intraformational conglomerates and silty sandstones from red to grey and greyish-green color. Intraformational conglomerates should be explained as a products formed by presettlement of siltstone pieces, formed as a result of variation of water level, which led to drying, breaking and dislocation of siltstone fragments and afterwards to the cohesion by sandy material.

Increased concentrations of organits matter uranium and sulphides of copper molybdenum, selenium and lead are observed in a zone of lithofacies alterations, which represents a space where sitly component becomes dominant in reference to sandy component. It should be emphasized that this relationship sandy component-sitly component extents in a N.E.-S.W. direction, that is in a direction of deepening of a basin.

General geological-tectonical situation and lithological-geochemical characteristics of mottled series, indicate that in this part of “Stara Planina” is present mildly sloped structure of artesian basin type, in whose proximity are located granite complex of Janja and crystalline schists with intrusions, dikes and veins of quartzporphyres, granodioriteporphyrites, porphyrites, quartzporphyrites and graniteporphyres. Mildley sloped structures consist of water permeable clastites of grey, greyish-green and grey-reddish color, which are located between red silty rocks. In certain part of the greyish, greyish-green and grey-reddish clastites are present distinguished changes of oxidation-reduction potential in an interval from +120mV up to -200mV, pH of the medium being 7.1-8.2 in these parts of the clastites of mottled series are present increased concentrations of uranium, organic matter, copper, molibden, selenium and lead. It should be emphasized that geochemical contrast coincides with direction of lithofacies alterations, that zone being of 150 m. of width. Generalized model of formation of deposits and occurrences of motteld sandstones, consists mainly of two phases. In the first phase uranium is being concentrated during the process of sedimentation. Uranium and other metals from crystalline schists, granites and paleovolcanics turn into solution and later on by geting in contact with organic matter in coastal shallow waters get reduced from solution and concentrate at the same time with the components of sedimentary rock. During the process of diagenesis redistribution of uranium takes place, as a result of infiltration process.

Atmospheric and underground waters that circulate in terrigenous sediments dissolve uranium compounds formed in a first phase in one part of the layer and concentrate new uranium compounds in other parts of the layer, where, for such an action favourable geochemical-lithological conditions exist, in a shape of flat ore bodies in which uranium occurs as a pitchblende as impregnations and thin veins, with a presence of considerable contents of copper minerals chalcopryite, bornite and chalcocite.

All of uranium occurrences in a mottled series are more or less similar by position and by mineral paragenesis except for the occurrences Gotousa which occurs in the upper part of the mottledseries and where, besides inconsiderable uranium content, considerable higher content of thorium and TiO_2 exist.

Occurrences of uranium in the Tertiary sediments on a N.W. brim of anticlinorium of “Stara Planina” are connected to the lake sediments of middle Miocene age, which are represented by conglomerates, sands, clays and marls with coal. Occurrences in “Mala Reka” near a contact with gneisses is represented by nodules of coal matter in conglomerates, increased concentrations of uranium being tied to coats over fractures in nodules. Occurrence of uranium in “Stitarska Reka” is connected to an outcrop of greenish-blue clays.

Part II: Possibility of In-situ leaching of Uranium ore

“In-situ” leaching (ISL), or solution mining, is a method of recovering minerals like uranium throughout boreholes drilled into the deposit. The process primarily involves drilling of holes into the ore deposit. Explosive or hydraulic fracturing may be used to create open pathways in the deposit for solution to penetrate.

The Microorganisms may be applied for removal of metals from ore bodies without practicing conventional mining. „In-situ“ mining, more attractive then conventional open pit and underground mining, has been used commercially to recover uranium.

Many problems, such as exposure to radon gas and mine roof failures are avoided with the „In-situ“ mining. However, other problems are created by the need to inject solutions into shallow aquifers. Restoration of the aquifer and ore body must be undertaken after the mining operation has ceased; injected chemicals and metals must be removed and immobilization processes and protection of the ore body must be carried out.

Ore body preparation for leaching

General questions that arise in research related to leaching process are connected to reagent consumption and leaching kinetics. With leaching “In-situ”, considering both these questions give an insight into most significant parameters: bacteria types and the conditions of their survival and the choice of most appropriate agents that increase the velocity of leaching. The extensive application in the field of bacteriological leaching have the *Tiobacillus Ferrooxidans* and *Thiobacillus Thiooxidans* due to nature of their life process based on mineral oxidation. The velocity of dissolution of uranium minerals is increasing by seven or more times.

The ore body should be divided into working blocks and safety pillars (Fig. 10 and 11). The height and the width of the blocks should be established on the basis of physical-mechanical properties of ore and accompanying rocks. Working blocks should be drilled, blasted with explosive mixture in dense medium, by height, width and depth in whole, in order to avoid the unnecessary extraction of certain quantity of the ore because of loosening coefficient increase, i.e. volume of the mined ore.

Conditions for in-situ leaching

Certain geological and hydrological criteria must be met before an ore body deposit is considered suitable for “In-situ” leaching:

- The ore should occur in a relatively impermeable stratum,
- The host rock should have a good permeability,
- The ore must be located below the water table,
- The direction and velocity of regional water flow must be known,
- The uranium minerals must be amenable to proposed dissolution,
- The ore body should be of sufficient size and grade to justify the cost of production.

Technique of “in-situ” leaching

Under favorable geological – hydrogeological conditions, the process of “In-situ” leaching is carried out by injecting the suitable solvent into the ore body through injection holes. The solvent is allowed to pass / flow through the ore body for desired period dissolving the desired metal content and the pregnant solution is then recovered through production well by pumping (Fig.11). The pumped out solution pass through normal hydrometallurgical route in which uranium is segregated.

Method of “In-situ” leach underground mining

“In-situ” leach mining entails pumping of a solution into the ore body via a borehole, which circulates via the porous rock dissolving the ore and is extracted by means of a second borehole. The leach solution differs according to the ore deposit - for salt deposits the leach may be fresh water into which salts may willingly dissolve. For copper, acids are generally required to improve solubility of the ore minerals within the solution. For uranium ores, the leach might be acid or sodium bicarbonate. Since “In-situ” leaching involves treating large quantities of ore and barren rock, the cost of leaching chemicals is an important consideration in the overall production cost of mining. Therefore leaching agent costs should be kept as low as possible. Among the reactants, sulphuric acid typically combines high leach performance and relatively low cost. Typical “In-situ” Leaching Operation (Image taken from <http://www.wise-and-uranium.org/uisl.html>) www.uraniumsa.org/.../insitu_leaching.htm.

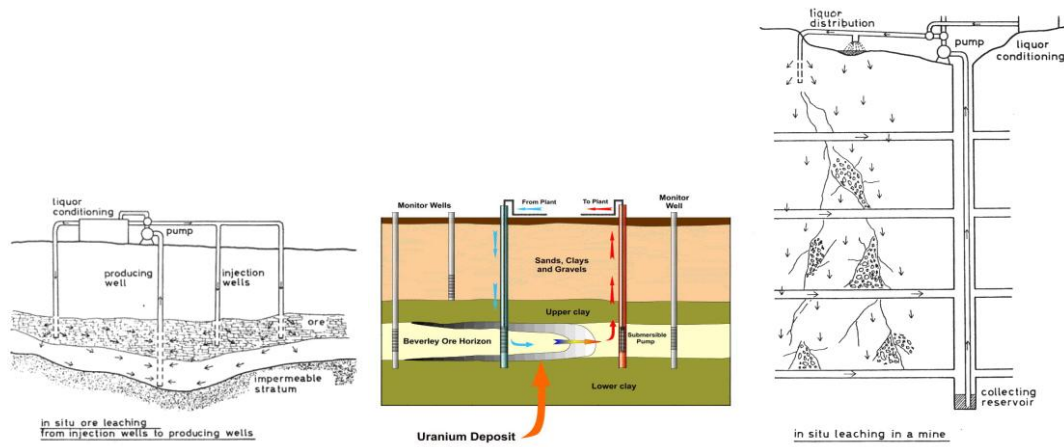


Fig. 10: Typical “In-Situ” Leaching Operation; (Three examples)

Leaching solution should be applied on the upper horizon in order to ensure solution migration through the blasted ore. By gravity means, leaching, as it passes through the ore, the solution should be moving on to the bottom of working block. Solution circulation should be ensured by solution collection at the bottom horizon and it's returning in the working block by pumping until the end of the leaching, as it is shown on Fig. 2.

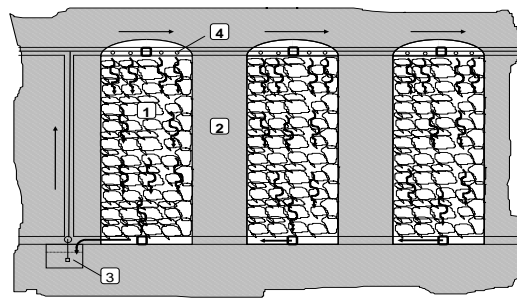


Fig. 11: Flowsheet of leaching solution migration and circulation through the blocked ore

1. Working block; 2. Safety pillar;
3. Reservoir for liquor with pump 4. Sprayers

Very simplified scheme of uranium ore leaching process resulting in yellow cake is presented in Fig. 3.

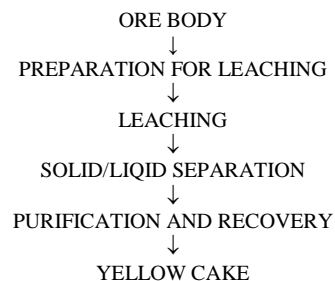
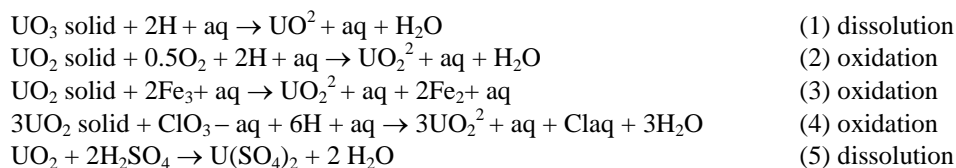


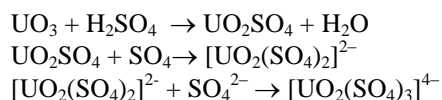
Fig. 12: Unit operations in uranium ore processing

Chemical reactions in sulphuric acid leaching

The interactions of uranium oxide using the sulfuric acid leaching method may be presented as follows:



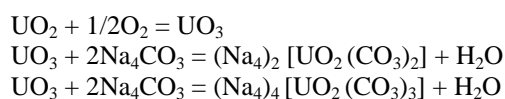
Leaching of ores containing hexavalent uranium results in the formation of various uranyl sulphate complexes in solution:



The concentration of the various anions in solution is determined by the pH value, as well as by the concentration of the sulphate ion and uranium. Uranium ores generally contain considerable quantities of tetravalent uranium which is difficult to leach without an oxidizer.

Chemical reactions in alkaline leaching

Alkaline (carbonate) leaching is based on the ability of the hexavalent uranium to form very soluble complexes in weakly alkaline media. The carbon dioxide reacts with the natural carbonates in the host rock to generate dissolved bicarbonates and carbonates at a neutral or slightly alkaline pH. The equations of the reactions for the leaching of uranium with sodium salts are presented below:



If the sulphide concentration exceeds 2–4%, carbonate leaching becomes unprofitable, and the risk of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) precipitation becomes very high. This can cause irreversible plugging of the host rock.

In contrast to an acid system, oxygen slowly oxidizes tetravalent uranium in an alkaline environment. The dissolved oxygen concentration in the injection fluid is limited by its solubility, and hence, by the available hydrostatic pressure on the host rock. As a result, the carbonate leaching can benefit from using hydrogen peroxide as a means to increase the concentration of oxygen delivered to the ore deposit. In the carbonate environment, this compound easily decomposes and releases oxygen, which oxidizes tetravalent uranium to the hexavalent state. Factors determining the choice between acid or alkaline in-situ leaching technology are:

- composition of the host rock and ores,
- reagent cost and consumption,
- degree of uranium recovery and the intensity of the process.

For economic sulphuric acid leaching the carbonate content should not exceed 2% CO_2 . The ores with higher carbonate content normally require alkaline (bicarbonate) leaching.

Processing of solutions

The production solutions recovered from ISL, contrary to the liquid phase from milling plant technology, are characterized as follows:

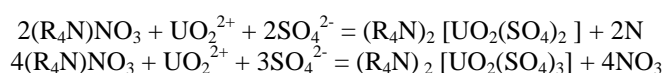
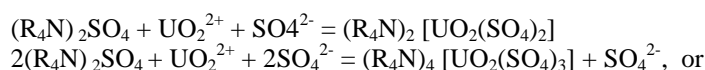
- a relatively low uranium concentration
- a more complicated chemical composition,
- complete closed mode of solution recycling without any remove of salts.

The complex ions $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ and $[\text{UO}_2(\text{SO}_4)_3]^{4-}$ can be sorbed from their respective leach solutions by ion-exchange resins. Conventionally, sodium and ammonium chloride or nitrate solutions are then used to elute the sorbed uranium from the exchange resins.

Uranium can also be removed from acidic ore leach-liquors through solvent extraction. As a general rule, solvent extraction is preferred over ion-exchange methods for acidic solution containing more than one gram of uranium per litre. Solvent extraction is not useful for recovery of uranium from carbonate leach liquors, however.

More uranium has been produced using extraction with organic solutions or strong-base ion-exchange as the primary method of purification than by any other process.

The selectivity with which strong-base anion exchange resins absorb uranyl sulphate complexes from solution is well documented. The process of uranium adsorption from leaching solutions onto strong base anionic resin is described by equations:



The ion-exchange process can be divided into several independent stages following one another in time and space:

- The diffusion of the adsorbed ion through the interface (boundary layer) film;
- Its migration from the resin surface to any point within its volume;
- The ion-exchanging or adsorption interaction at an active site;
- The migration of the displaced ion from the exchange site to the contact surface;
- Diffusion of the displaced ion through the interface (boundary layer) film into the barren solution.

Precipitation of yellow cake

Prior to final purification, uranium present in acidic solutions produced by the ion-exchange or solvent-extraction processes described above, as well as uranium dissolved in carbonate ore leach solutions, is typically precipitated as a polyuranate. From acidic solutions, uranium is precipitated by addition of neutralizers such as sodium hydroxide, magnesia, or (most commonly) aqueous ammonia. Uranium is usually precipitated as ammonium diuranate, $(\text{NH}_4)_2\text{U}_2\text{O}_7$. From alkaline solutions, uranium is most often precipitated by addition of sodium hydroxide, producing an insoluble sodium diuranate, $\text{Na}_2\text{U}_2\text{O}_7$. It can also be precipitated by acidification (to remove carbon dioxide) and then neutralization (to remove the uranium) or by reduction to less soluble tetravalent uranium. The final uranium precipitate, commonly referred to as yellow cake, is dried. In all cases, the yellow cake contains 70 to 90% of uranium oxide.

Environmental Impacts

The advantages of this technology are: the reduced hazards for the employees from accidents, dust, and radiation, the low cost; no need for large uranium mill tailings deposits.

The disadvantages of the “In-situ” leaching technology are: the risk of spreading of leaching liquid outside of the uranium deposit, involving subsequent groundwater contamination; the unpredictable impact of the leaching liquid on the rock of the deposit; the impossibility of restoring natural groundwater conditions after completion of the leaching operations.

After termination of an “In-situ” leaching operation, the waste slurries produced must be safely disposed, and the aquifer, contaminated from the leaching activities, must be restored. Groundwater restoration is a very tedious process that is not yet fully understood. So far, it is not possible to restore groundwater quality to previous conditions.

Specific requirements for restoration of the ore body have been established. To avoid possible contamination of adjacent aquifers, monitoring wells are required so that any lixiviant escaping from the region designated for leaching can be quickly detected. Bacteria, ubiquitous in the overlying soil, can also be present.

Several in situ mining operations have experienced decreased production due to heavy accumulations of inorganic particles and bacteria on well screens, casings, and submersible pumps. Microorganisms isolated from the „In-situ“ uranium leaching environment were identified as aerobic, heterotrophic organisms commonly found in the soil.

Conclusion

With steady implementation of country's nuclear power program, the demand for large production of uranium at competitive cost may rise over the years. On favorable geologic and hydrologic conditions, some of the low-grade occurrences in Serbia may find favor for “In-situ” leaching due to inherent advantages of the system like low gestation period, low cost technology, low operating cost and potential for adjusting the production to match the requirement.

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