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Some Historical Briefs and Outlooks of the Chemical and Biological Acid Leaching of Uranium Ores

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ABSTRACT

The purpose of this paper is to briefly review early developments in the chemical and biological acid leaching of uranium ores in Portugal, Canada, Sweden, Finland, Estonia, and Pakistan. Uranium exists in tetravalent (U(IV)) and hexavalent (U(VI)) oxidation states in igneous, metamorphic, and sedimentary mineral deposits. Acidic ferric sulfate is a chemical oxidant of tetravalent uranium and is regenerated from ferrous iron in the leachate and produced also from pyrite (FeS_2, cubic), marcasite (FeS_2, orthorhombic), greigite (Fe_3S_4) and pyrrhotite ($Fe_{1-x}S$) by acidophilic Fe- and S-oxidizing bacteria and archaea. The hexavalent uranium is soluble in sulfuric acid solution (lixiviant) and is recovered in downstream hydrometallurgical processing to produce a concentrate (yellowcake). The acid bioleaching reactions are optimal at pH 1.5-3 as the low pH facilitates proton attack on minerals and alleviates the precipitation of metals in the leachate and on mineral surfaces. Uranium is extracted from ores on a commercial scale using heap, dump, and stope leaching processes. In some operations other metals can also be recovered as byproducts in the process.

Keywords: *Acid leaching, Acidophilic Microbes, Bioleaching, Pyrite Oxidation, Uranium Leaching*

1. Introduction

Uranium deposits occur in igneous, metamorphic and sedimentary rock types are widespread, with the largest deposits found in Australia, Kazakhstan and Canada [1-3]. To date, the largest high-grade uranium deposits containing 13.88%-15.92% U_3O_8 occur in the Athabasca Basin of northern Saskatchewan, Canada (Cigar Lake) [4, 5]. Uranium ore deposits are generally classified into 15 main categories of deposit types, each with multiple subtypes, according to their geological setting and genesis of mineralization and arranged by to their approximate economic significance [6]. About 40% of the uranium reserves are in sandstone type uranium ore deposits [7]. Almost 300 uranium minerals have been identified in the form of halides, oxides, carbonates, sulfates, phosphates, arsenates, vanadates, and silicates [8, 9]. Uranium also exists in organic complexes such as thucholite and uranyl oxalate minerals uroxcite and metauroxcite [10]. Some major and minor uranium-producing countries are presently Australia, Canada, China, India, Kazakhstan, Namibia, Nigeria, Pakistan, Russia, South Africa, Ukraine, United States and Uzbekistan [1]. According to the World Nuclear Association, the top four uranium producers in the world in 2021 ranked Kazakhstan, Namibia, Canada, and Australia.

Uranium can be extracted from ores with sulfuric acid (H_2SO_4) or carbonate solution ($NaHCO_3$, Na_2CO_3, NH_4HCO_3, $(NH_4)_2CO_3$, K_2CO_3, $KHCO_3$). Biological leach solutions with acidophilic iron- and sulfur-oxidizing autotrophs can also be used for the extraction of uranium from ores. In the leaching process, uranyl ion (UO_2^{2+}) forms soluble sulfate ($UO_2(SO_4)_3^{4-}$) or carbonate ($UO_2(CO_3)_3^{4-}$) complexes. The role of acidophilic iron- and sulfur-oxidizing mesophiles and thermophiles, archaea, and iron-oxidizing heterotrophs in the bioleaching of uranium ores is well documented and reviewed in the literature [11-15]. In the bioleaching process, dilute sulfuric acid is the leach solution promoting proton attack and ferric iron is the oxidizing agent. If uranium is initially present in the insoluble tetravalent state (U(IV)) in the ore, Fe^{3+} in sulfuric acid solution oxidizes it to U(VI), dissolving it as soluble UO_2^{2+}. Fe^{3+} is reduced to Fe^{2+} in this redox reaction and is re-oxidized by iron- and sulfur-oxidizing acidophilic bacteria and archaea [16-18]. An example of a flow sheet diagram of the bioleaching of uranium is shown in Fig. 1.

Depending on the specific grade and mineralogy of the ore body, the use of acidophilic iron- and sulfur-oxidizing bacteria in the industrial-scale extraction of uranium from ores containing pyrite and/or other sulfide minerals may be a feasible, alternative approach to the chemical hydrometallurgical process technology. Heap and dump leaching processes are technically feasible for bioleach operations, whereas the bioleaching of uranium is not practiced in stirred tank processes in commercial scale. The technology is particularly applicable to low-grade uranium ores (≤0.042% U), which contain pyrite or other sulfide minerals. The leaching process may be amended with pyrite or sulfur for the acidophilic iron- and sulfur-oxidizing bacteria to provide for oxidation and acid capacity of the leach solution [19, 20].

Many countries have had research groups working on uranium bioleaching projects using bench-scale, pilot-scale, and commercial-scale techniques with varying successes. These projects were primarily evaluating uranium leaching yields with changes in physical and chemical experimental conditions. The underlying microbiology of the leaching process was relatively poorly understood in the 1950's-1960's. Key enzymes, taxonomic and phylogenetic diversity, and molecular biological analysis of microbial cultures were practically unknown in the first 15-20 years of the emerging bioleaching technology. The domain Archaea was not discovered until 1977 [21]. The fundamental discovery and

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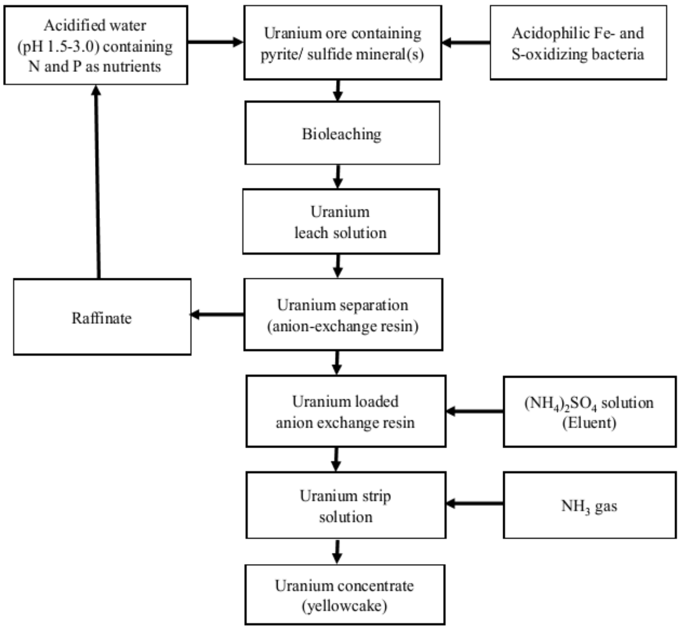

Fig. 1: An example of a flow sheet diagram showing bioleaching of uranium from ore to produce uranium concentrate (yellowcake).

emergence of molecular biology and omics have led in subsequent years to information on acidophilic thermophiles that are potentially useful in bioleaching processes at elevated temperatures.

The purpose of this paper is to review brief historical aspects, starting in the 1950's, of the chemical and biological leaching of uranium from ores in several countries including Pakistan. The history of the acid bioleaching of uranium coincides with R&D in the bioleaching of sulfidic ores for the extraction of copper, which was subsequently expanded to nickel, cobalt, and zinc. One driving force in boosting uranium extraction from ores in the 1950's-1960's especially and gradually ebbing through 1990, was the Cold War and stockpiling of nuclear weapons for nuclear deterrence. Uranium is now mostly used as fuel for nuclear power plants and nuclear reactors in naval vessels and as a source of isotopes in medicine, many industrial processes, and military purposes. The non-fissile U-238 isotope with a >99% relative abundance is the most common in nature.

Portugal

Early advances in the bioleaching of uranium ores date back to the 1950's. It was reported that the Urgeiriça uranium ore-processing plant in Portugal was not achieving the expected yield of uranium from the ore stockpiles [22]. The discrepancy in terms of the loss of uranium was eventually attributed to substantial leaching of uranium caused by rainwater. Subsequently, it was discovered that uranium dissolution from the ore was catalyzed by acidophilic Fe- and S-oxidizing autotrophs [23]. The Urgeiriça uranium ore contained, on average, 5% pyrite, which was oxidized by bacteria to acidic ferric sulfate lixiviant. In the 1950's, some studies on uranium bioleaching processes were initially directed towards preventing dissolution of uranium from ore, but it soon became apparent that this process could be applied to extract uranium from low-grade ores. In 1952-1953, a heap leaching process was started for the recovery of uranium on commercial scale at the Urgeiriça plant site. The Urgeiriça is one of the early milestones in the bioleaching of uranium ores [24]. Multiple small mines were active in mining uranium ores through 1962. In subsequent years, uranium mining did not employ specifically designed bioleaching processes with native bacteria, but heap leaching was practiced for low-grade ores [24]. Uranium mining in Portugal ceased in 2001.

Canada

In the 1960's, bioleaching processes were applied for commercial scale uranium extraction by heap, dump, and stope-leaching of mine waste rocks and worked-out stopes in uranium mines in the Elliot Lake area, Ontario, Canada [25-27]. The uranium mine waters containing acidic ferric sulfate were circulated through surface heaps and underground-stopes [28, 29]. Some mines leached uranium by hosing down roofs, walls, and floors of mine stopes at intervals of several months, because supporting underground structures could not be safely mined via conventional processing. Other left-behind uranium ore materials and waste piles were also treated with mine waters at acidic pH 2-3, yielding dissolved uranium at concentrations that were economically recoverable by using a strong basic anion ion-exchange resin [Amberlite IRA-400 (OH^-)].

The Agnew Lake Mine (Ontario) was the first operation where uranium bioleaching process was applied to a virgin orebody. Full-scale operation at the Agnew Lake Mine was launched in 1976 [30]. In the first year of stope leaching operations, the mine shafts and chambers were fill with the leachate. The underground and stope leaching works were discontinued in 1980 as fractures in the orebody failed to prevent the loss of leach solution. The surface heap bioleaching continued until 1985 [31]. Tailings in some uranium mines contain light and heavy rare earth elements in addition to other metals. In recent years, this has prompted interest in recovering rare earth elements from tailings by acid and bacterial leaching in abandoned or inactive uranium mines [32, 33]. In some mines, for example, yttrium could also be recovered as by-product from the raffinate solutions, which further improves the overall process economics.

Sweden

In Sweden, the alum-shale fields in the southern part are among the largest uranium-containing shale deposits in the world. Uranium ore from the alum-shale orebody was processed in the Ranstad mine during 1965-1969 [34]. The process was based on the leaching of uranium with sulfuric acid, yielding about 182 t U [35]. Weathering of the ore outdoors for weeks before the leaching process decreased the pyrite content and increased the subsequent yield of uranium by about 10%, but addition of bacteria was not tested in the process. Bacterial leaching of uranium from the alum-shale was tentatively tested in a laboratory-scale [36], but the research did not proceed to further experiments or optimization. After the mine closure, the site was eventually reclaimed, but analyses of drainage from pyritic materials at the site have shown acidic, sulfate-rich drainage, Fe(III) precipitation, and dissolved metals [37].

Bhatti [38] reported that 68-76% yield of U was obtained in stirred tank leaching of samples of black shale from the Kyrk Tåsjö deposit in central Sweden using mixed cultures of Fe- and S-oxidizing bacteria with 15-20 days of contact time. Uranium is also associated with the organic-rich fraction of the shale. Kalinowsky et al. [39] showed that uranium is dissolved from alum shale in *Pseudomonas* cultures. This was attributed to uranium sequestration with pyoverdine (a *Pseudomonas* protein) as well as microbial decomposition of the organic fraction of the shale, thus causing uranium dissolution.

In 1976, the Swedish government announced that uranium mining and production in large-scale were not compatible with Sweden’s nuclear policy, thus causing major shifts in uranium exploration and processing. Uranium mining in Sweden was banned in August 2018, with consequent financial losses of pending and planned uranium mining projects. There has been continuing commercial interest in exploring Swedish uranium-containing shale deposits [40], presumably for metals such as nickel and rare earth elements for which there is a high global demand. Uranium-rich alum shales (0.005-0.04% U) occur in Skåne, Västergötland, Östergötland, Öland, Närke and along the Swedish mountain range [41, 42]. In Häggån, for example, the large black shale uranium field in central Sweden is claimed to be the second largest undeveloped uranium resource in the world, also containing Mo, Ni, V and Zn [43, 44].

Finland

In Finland, uranium was produced in 1958-1961 in pilot-scale in the Paukkajanvaara mine (North Karelia) using sulfuric acid as the lixiviant [45]. A total of 40,000 t ore was excavated yielding about 30 t U before the uranium rich section was depleted. The process was not designed for native bacteria to accelerate the leaching. Thirty years later, the mine site was reclaimed, and field research revealed typical acid mine drainage at the mine site, evidence for microbial oxidation of residual Fe-sulfides exposed to humidity, rainwater, and air and the site has an established microbial community [46]. Reconnaissance and environmental sampling have been implemented to monitor the release of radionuclides and base metals from the mine site [47-49].

In 2007, the Terrafame Ltd. (called Talvivaara Ltd. at that time) mining company started a bioheap leaching process to recover Ni, Co, Cu, and Zn from a black schist ore in the Kainuu region [50-53]. Since then, in the intervening years, the company secured a permit to also recover uranium from the leach solution cycle. Terrafame Ltd. is now in the process of optimizing uranium recovery for full-scale operation (200 t U/year) in 2024 from the leach solution cycle at the mine site (www.terrafame.com). Uranium recovery is additional to the Ni, Zn, Cu, and Co concentrates already produced in the bioheap leaching operation. The plan is to initiate uranium production alongside the production of other metals throughout the operating period, which covers at least the next 30 years. The black schist mineralization contains about 0.0017% U, some of it as thucholite. The grade is not sufficient to be classified as uranium ore, nor could it economically support uranium mining as the sole product. The bioheap plant is in the boreal climate with snow cover during the winter, but the winter and snow have little effect on the microbial activity in the interior zones of the heaps due to intense exothermic oxidation of sulfide minerals.

Estonia

In Estonia, the Sillamäe metallurgical plant processed uranium ores for the Soviet nuclear program, starting in the mid-1940’s. Sillamäe is on the southern coast of the Gulf of Finland, at the mouth of the Sõtke River. The history of the uranium plant processing graptolite-argillite ore has been reviewed by Lippmaa and Maremäe [54-56] and Hade and Soesoo [57]. The plant also processed uranium ores shipped from eastern and central European countries until 1977. In 1960-1963 the Sillamäe plant tested the bacterial leaching of uranium from graptolite-argillite ore in open air heaps and a large outdoor 2,000-ton concrete percolator reactor as well as in wooden percolators with shelves over 23 months. The yields of uranium leaching decreased with increasing particle size: 55% U with 25 mm and 33% with 50 mm material. For reference, 1% leaching of uranium was noted with 100-200 mm lumps over 18 months [54, 58, 59]. No follow-up test work on the bacterial leaching was announced. The plant subsequently tested the pressure leaching of uranium, but the results did not justify uranium processing in commercial scale and the funding was finally discontinued in 1973. The graptolite-argillite mineralization in northern Estonia is a potential resource of many metals in addition to uranium [60, 61]. Anaerobic decomposition of organometallic complexes can also release some metals in the solution phase [62, 63].

The metals in the shales are, however, of low grades and commercial processing with conventional hydrometallurgy or bioleaching is presently not economically feasible.

Pakistan

In Pakistan, polymetallic black shale deposits represent potential uranium reserves. For example, uranium deposits in Pakistan have been summarized by Butt [64], Mansoor [65] and Akhtar et al. [66]. Shake flasks bioleaching experiments with a mixed culture of Fe- and S-oxidizing bacteria performed at 50% pulp density of a black shale sample containing 0.0042% U solubilized 76-80% U in 30 days of contact time [67]. Uranium dissolution from the shale was mainly attributed to Fe^{3+}, >500 mV redox potential, and low pH 1.5-1.9 in the leach solution. Uranium from the Baghalchur low-grade sandstone ore (0.023% U) amended with elemental sulfur and/or sulfur mud was leached by acidophilic autotrophs in shake flasks, columns, and small pilot-scale bioheap studies [68, 69]. Bacterial oxidation of sulfur generated sulfuric acid as lixiviant for uranium solubilization from the sandstone ore.

Reddish-brown Fe(III)-precipitates collected from the water channels of the bed-rock seepage in the black shale formation of Chamiari (Ghazi Tarbela) and Kala Katha area of District Haripur, Khyber Pakhtunkhwa (Pakistan) are shown in Fig. 2. Such precipitates are attributed to the microbiological iron and pyrite oxidation in black shales, with subsequent ferric iron precipitation as Fe(III)-hydroxysulfates. The precipitates are mixed jarosite types (solid solutions of jarosite) and schwertmannite. Fe(III)-precipitates sequester and retain dissolved uranium from mine drainage, shown as an example in the chemical analysis in Table 1. The mechanism of uranium sorption by iron precipitates is not clear.

Table 1: Uranium content of iron precipitates collected from the seepage channels of black shale bedrock in Chamiari (Ghazi, Tarbela), Khyber Pakhtunkhwa (Pakistan). All samples were reddish-brown Fe(III)-hydroxysulfate precipitates (unpublished data, T.M. Bhatti).

Sample No.	Description of sample	U content (ppm)
SW-1	Water channel	13
SW-2	Seepage of shale bed rock	109
CHW-2	Seepage of shale bed rock	9
CHW-3	Seepage of shale bed rock	46

Pakistan has reserves of uranium mineral resources locked up in black shales and sandstone type deposits. Uraniferous black shales are widely distributed in the Precambrian sediments in Khyber Pakhtunkhwa Province and adjoining areas of Azad Jammu and Kashmir [70-72]. The black shales contain abundant organic matter (kerogen), disseminated fresh, tiny, and large crystals of pyrite (7-10%) and U, Ni, V, Zn, and rare earth elements. The black shales in the Manki Formation, Ghandgarh Range, near Ghazi-Tarbela (Khyber Pakhtunkhwa) contain on average 0.0042-0.006% U [73].

Fig. 2: Acid mine drainage representing bacterial oxidation of pyrite and sulfide minerals in the black shale formation of Chamiari (Ghazi Tarbela) and Kala Katha, Khyber Pakhtunkhwa (Pakistan). The arrows point at the formation of red-brownish Fe(III)-precipitation in the mine drainage.

In general, shale deposits are considered as polymetallic with variable content of pyrite and other sulfide minerals, sometimes also carbonate nodules or layers. Some mineralizations are enriched in Ag, Mo, Zn, Ni, Cu, Cr, V and less commonly Co, Se, and U [41, 43, 44, 74]. The weathering causes changes in the elemental and mineralogical composition in black shale deposits and leads to elevated concentrations of metals and sulfates in surface water and stream sediments. Metal-bearing minerals and metals are interspersed in the organic fraction in the shale-matrix. Based on the weathered bedrock/soil profiles, disintegration is initiated with the oxidation of pyrite and organic matter, which increase the overall porosity and water penetration. Prolonged exposure of black shales and coal-seams to rainwater, humidity, and air promotes the oxidation of pyrite and other Fe-sulfides to elemental S, thiosulfate, polythionates and sulfates, typically mediated by native acidophilic iron- and sulfur-oxidizing bacteria in sulfidic mine sites.

Conclusion

Since the initial uranium bioleaching studies in the early 1950’s, applications of acidophilic microbes for recovering uranium from various minerals, ores and rocks have been tested in several countries. Historically, the Cold War boosted the uranium production often without regard to environmental safeguards, and the environmental and human health legacies of this era are still apparent in many inactive and abandoned mine sites worldwide. Major advances have been made in the understanding of the kinetics of bacterial activities and leaching reactions as well as electrochemical basis of mineral dissolution. Indigenous bacteria and their communities in uranium mine sites have been characterized and new species have been discovered. The flux of molecular and genetic knowledge of microbial biochemistry and physiology has discovered insights on microbe-mineral interactions and regulatory mechanisms underlying microbial responses for example to dissolved metals and other stress and inhibitory factors, permissive temperature ranges, substrates, nutrients, and microbial population dynamics. Such biological parameters affect bacterial efficacy in the leaching process and are targets for optimization with fine tuning for specific ore or rock types. Mineral composition and galvanic coupling, particle size distribution, pulp density, aeration, and ore/rock permeability are some examples of the physical parameters that must be considered for engineering design in the leaching process. The bioleaching-based technology is particularly suited for low-grade uranium ores, which are economically marginal or otherwise difficult to process by conventional hydrometallurgy. Scientific discoveries, R&D priorities, collaborations, and economic incentives to further the biotechnology of mineral processing are regularly discussed in the biennial International Biohydrometallurgy Symposium (IBS) series. This is an international forum and meeting place for scientists and other specialists as well as the industry representatives with wide backgrounds to address critical issues in the mineral biotechnology. Similarly, the European Union has sponsored international programs such as BIOSHALE, BIOMINE, and BIOMOre, which have promoted collaborative problem-solving, troubleshooting, and research efforts. Bioleaching technology requires inputs from many disciplines, requiring cooperation, training, and funding as well as skilled scientists and engineers collaborating with the mining industry.

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