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GENERATION OF ACID DRAINAGE IN AN URANIUM ORE DEPOSIT

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ABSTRACT: The mining operations in the uranium deposit Curilo were ended in 1990 but since that time the deposit is a permanent source of acid drainage waters. These waters have a low pH (usually in the range of 2-3) and contain uranium, radium, some toxic heavy metals, arsenic and sulphates as main pollutants. The concentrations of these pollutants are usually 2-5 times higher than the relevant permissible levels. The waters are generated as a result of bacterial oxidation of the residual amounts of pyrite, other sulphides and uranium minerals present in the abandoned open-pit and underground mining works as well as in some dumps consisting of rock mass and low-grade ores. Some data about the generation of acid drainage waters after rainfall in such a dump are shown in this paper. It was found that the dump was inhabited by a varied microflora in which different chemolithotrophic bacteria were the prevalent microorganisms. The influence of some essential environmental factors such as pH, temperature, and water, oxygen and nutrient contents of the dump on the microbial activity was established.

Key words: bacterial leaching, chemolithotrophic bacteria, radioactive elements, toxic heavy metals

INTRODUCTION

The uranium deposit Curilo is located in Western Bulgaria, about 35 km north from Sofia. For a long period of time this deposit was a site of intensive mining activities including both the open-pit and underground mining techniques as well as the in situ leaching of uranium. The ore was rich in pyrite and, apart from uranium, contained some non-ferrous metals such as copper, zinc and lead. The mining operations in the deposit were ended in 1990 but since that time the deposit is a permanent source of acid mine drainage waters. These waters have a low pH (usually in the range of 2 - 3) and contain uranium, radium, some heavy metals (mainly iron, manganese, copper, zinc, lead), arsenic and sulphates as main pollutants. The concentrations of these pollutants are usually 2 - 5 times higher than the relevant permissible levels for waters intended for use in agriculture and/or industry.

There are three main sources of such polluted waters in the deposit:

– permanent groundwaters arising after the closure of the underground mine and coming from the underground mining works. At present, these waters are effluents from a gallery (mentioned as No 5) which is located about 170 m beneath the bottom of the former open-pit mine. In 1985 the ore layers located to a depth of about 15 m from the bottom of the open-pit mine were crushed by means of explosives and were subjected to in situ leaching until 1990;

– drainage waters arising after rainfall from the 15 m ore zone. These waters are also effluents from the gallery No5;

– drainage waters arising after rainfall from some dumps consisting of mine wastes and low-grade ores.

Most of the above-mentioned waters are collected in a ravine located near the gallery No 5. This ravine reaches a small river (named Teina), where the polluted waters from the deposit are mixed with the waters of the Teina. Approximately 1.5 km from this point, the river Teina flows into the great river Iskar.

The present paper contains some data from a study on the generation after rainfall of acid drainage waters in a dump located near the above-mentioned ravine. Such data are necessary for further investigation connected with the possibilities to cleanup the polluted waters or to prevent their generation.

MATERIALS AND METHODS

The ore dump used as an experimental plot in this study was formed on a moderately steep hill without any ground preparation. The material placed on the dump was run-of-mine material and included different ore sizes - from very fine particles (less than 100 microns) to boulders as large as 0.2 - 0.3 m in diameter. The dump contained about 80000 tons of ore.

Pyrite was the main ore mineral in the dump. Chalcopyrite was the main copper-bearing mineral but some secondary copper sulphides such as covellite, chalcocite and bornite were also present, together with some copper oxide minerals. Sphalerite, galena and arsenopyrite were present but in lower concentrations than chalcopyrite. The main uranium-bearing minerals in the ore were nasturane, torbernite, metatorbernite, pich-blende, metaotunite and basetite. Quartz was the main mineral of the host rock. Clay minerals and oxidation

The quality of the dump effluents was monitored at least once per month in the period May 2000 - April 2001. The parameters measured in situ induced pH, Eh, dissolved oxygen, total dissolved solids and temperature. Elemental analyses were done by atomic absorption spectrophotometry and induced coupled plasma spectrophotometry in the laboratory. The radioactivity of the samples was measured, using the solid residues remaining after their evaporation, by means of a low background gamma - spectrophotometer ORTEC (HpGe - detector with a high distinguishing ability). The specific activity of Ra-226 was measured using a 10 l ionization chamber. The total β-activity was measured by a low background instrument UMF - 1500M.

The procedures for collecting liquid or solid samples for microbiological analysis and the procedures for isolation, identification and enumeration of different microorganisms have been described elsewhere (Karavaiko et al., 1988; Groudeva et al., 1993).

The ability of the indigenous microorganisms to generate acid drainage waters was studied under laboratory conditions by leaching a composite sample of the dump material. Data about the chemical composition and some essential geotechnical parameters of this sample are shown in Table 1. Data about radiological characteristics of the ore are shown in Table 2. The leaching was carried out in PVC percolation columns with an effective length of 1800 mm and a 105 mm internal diameter. Each column was charged with 30 kg of fresh ore used within 24 h after its collection from the dump. The ore contained viable microflora and was crushed to less than 10 mm in size.

Table 1. Data about the chemical composition and some geotechnical parameters of the ore used in this study

Parameters	Value
Chemical composition	
– SiO_2	68.4 %
– Fe_2O_3	10.4 %
– Al_2O_3	4.82 %
– CaO	0.32 %
– MgO	0.17 %
– S total	0.95 %
– S suphidic	0.64 %
– U	114 g/t
– Cu	842 g/t
– Zn	312 g/t
– Pb	410 g/t
– As	123 g/t
pH (H_2O)	2.8
Net neutralization potential	-23 kg $CaCO_3$/t
Bulk density	1.63 g/cm^3
Specific density	2.84 g/cm^3
Porosity	41 %
Permeability	8x10^{-2} m/s

Table 2. Radiological characteristics of the ore

Component	Nuclide specific activity, Bq/kg
^{238}U	1410
^{226}Ra	1850
^{232}Th	170
^{40}K	680

Distilled water was pumped to the tops of the columns at rates varying in the range of 50 - 200 l/ton ore per 24 h. In some cases $(NH_4)_2SO_4$ and KH_2PO_4 were added to the leach solutions to produce final concentration of about 0.10 - 0.50 and 0.03 - 0.10 g/l, respectively. The pregnant column effluents were recycled to the tops of the columns and were circulated in this way allowing heavy metals, arsenic and sulphate to accumulate.

Analysis of the circulating solution for ferrous, ferric and total iron species, dissolved heavy metals and arsenic, sulphate ions, pH, Eh and number of iron-oxidizing chemolithotrophic bacteria followed the progress of the bacterial leaching,

The bacterial activity in situ in the dump was determined by following the rates of ferrous iron oxidation in samples of drainage waters collected from different sections of the dump as well as in 9K nutrient medium (Silverman and Lundgren, 1959) inoculated with freshly collected ore samples. These experiments were carried out in 300 ml Erlenmeyer flasks containing 100 different depths in the dump, at the relevant natural temperatures, for 5 days. The technique described by Karavaiko and Moshniakova (1971) was used with some modification (Groudev and Groudeva, 1993) to determine the $^{14}CO_2$ fixation in situ.

RESULTS AND DISCUSSION

Data about the quality of the drainage waters, which flowed out from the dump, are shown in Table 3. The flow rate of these waters varied in the range of about 0 - 23 m^3/24 h.

ml liquid phase. The flasks were incubated in situ, at also found in zones with temperatures in the range of 10 - 40°C, although in lower numbers than the mesophilic chemolithotrops. The extremely thermophilic chemolithotrophic bacteria related to the genera Sulfolobus and Acidianus were not detected in the dump and dump effluents. Several heterotrophic microorganisms were found but it seemed that only those related to the genus Acidiphilium were typical members of the microbial community inhabiting the aerobic zone of the dump. This zone reached depths of about 3 - 5 m from the surface. The distribution of the chemolithotrophic bacteria was mostly confined to the upper layers (the top 0.5 - 1 m) of the dump with densities as high as in excess of 10^8 bacteria/g of ore. The

Table 3. Data about the drainage waters from the dump

Parameters	Value	Permissible levels for waters used in agriculture and industry
Temperature, °C	(+6.4) – (+14.5)	-
pH	2.1 – 3.7	6 - 9
Eh, mV	+(370) – (+640)	-
Dissolved O_2, mg/l	0.8 – 2.5	2
Total dissolved solids, mg/l	1140 – 5100	1500
Solids, mg/l	44 – 135	100
Oxidativity (by $KMnO_4$), mg/l	2.1 – 7.0	40
Chemical oxygen demand (COD), mg/l	4.4 – 21	100
Biological oxygen demand (BOD_5), mg/l	1.4 – 4.1	25
SO_4^{2-}, mg/l	640 – 2844	400
U, mg/l	0.77 – 4.48	0.6
Ra, Bq/l	0.140 – 0.710	0.150
Cu, mg/l	1.45 – 9.43	0.5
Zn, mg/l	1.70 – 23.50	10
Pb, mg/l	0.25 – 0.82	0.2
Cd, mg/l	0.02 – 0.08	0.02
Mn, mg/l	1.5 – 14.00	0.8
Fe, mg/l	221 – 1405	5
As, mg/l	0.02 – 0.35	0.2

The generation of the drainage waters was connected with the oxidative activity of the acidophilic chemolithotrophic bacteria, which inhabited the ore dump (Table 4). Acidithiobacillus ferrooxidans was the most widely distributed and the most numerous microbial species. Some of the strains of this bacterium isolated from the dump differed markedly from each other with respect to their ability to oxidize sulphide minerals, ferrous iron and elemental sulphur as well as to their growth rate and yield and in the way they reacted to some environmental factors.

The chemolithotrophs Leptospirillum ferrooxidans and Thiobacillus thioooxidans were invariably found but almost always in lower numbers than A. ferrooxidans. Moderately thermophilic chemolithotrophic bacteria related to Sulfobacillus thermosulphidooxidans and the genus Thiobacillus were found mainly in some rich-in pyrite dump sections the moderate thermophiles were the prevalent microorganisms. These bacteria, however, were

number of chemolithotrophs decreased with increasing depth and in the anaerobic zone was negligible. In this zone the sulphate-reducing bacteria as well as bacteria able to reduce the Fe^{3+} and Mn^{4+} were found but their growth was limited due to the shortage of organic donors of electrons.

The results from the column leaching experiments revealed that the indigenous chemolithotrophic bacteria were able to leach efficiently pollutants from the dump material (Figure 1) and to produce drainage waters with composition similar to that of the drainage waters generated under natural conditions. It was found that the microbial activity depended on some essential environmental factors such as water and oxygen content in the ore mass, pH and composition of the waters percolating through the ore and level of the ambient temperature. It was possible to change this activity by suitable changes in the levels of these environmental factors. Thus, the improvement of the natural aeration of the ore by using an interrupted irrigation rate with rest periods in the solution supply to the ore as well as the addition of nutrients (ammonium and phosphate ions) to the leach solution enhanced considerably the efficiency of leaching. On the other hand, the increase in the pH of the leach system to the neutral point by addition of crushed limestone, the addition of toxic agents such as mercury ions and biocide to the leach solution and the isolation of the ore surface by a clay layer to prevent the access of water and air to the ore material in the columns inhibited the microbial activity and the generation of acid drainage waters.

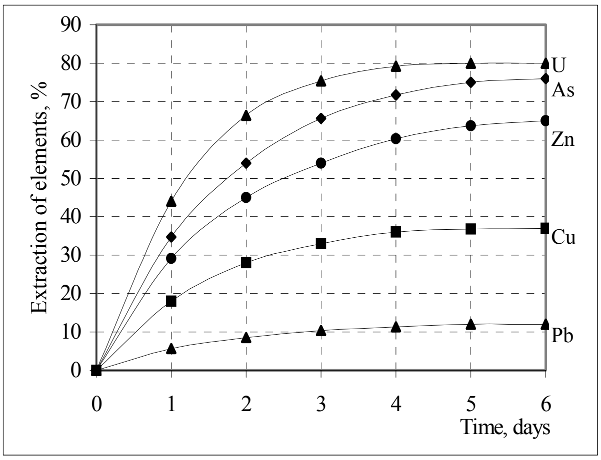

Fig. 1. Bacterial leaching of pollutants from dump ore in percolation columns.

Table 4. Microflora of the dump effluents

Microorganisms	Cells/ml
Mesophilic iron-oxidizing chemolithotrophic bacteria (Acidithiobacillus ferrooxidans, Leptospirillum ferrooxidans)	10^4 - 10^8
Moderately thermophilic chemolithotrophic bacteria (Thiobacillus spp, Sulfobacillus thermosulfidooxidans)	10^2 - 10^6
Extremely thermophilic chemolithotrophic bacteria (Sulfolobus, Acidianus)	0
Heterotrophic bacteria (mainly such related to the genus Acidiphilium)	10^1 - 10^3
Fungi	1 - 10^3
Protozoa	0 - 10^2

The results from the laboratory experiments were confirmed by the data about the determination of the bacterial activity in situ in the dump (Table 5). The highest bacterial activity was observed in zones with a water content of about 30 - 35 %. After heavy rainfall the bacterial densities in dump effluents decreased but the total amount of bacteria washed out from the dump increased. Usually, bacterial numbers and activity were elevated after rest (dry) periods in dump irrigation. This was connected with the mass transfer of oxygen and fluxes of reactants and products within the ore mass. In zones, in which the content of oxygen in pore solutions was low (less than 1 mg/l) the bacterial activity also was low. The highest activity was measured in zones with a pH in the range of about 1.5 - 2.5. In zones with pH higher than 3.5 - 4 both the number and activity of the acidophilic chemolithotrophs were relatively low. The addition of ammonium and phosphate ions to the dump had only a slight positive effect on the number of chemolithotrophs and on the leaching rates. This was due to the fact that the natural concentration of these ions, although relatively low (less than 10 mg/l for each of the ions), were sufficient to maintain the bacterial growth and activity under the real dump conditions.

The temperature inside the dump varied during the different climatic seasons only within a relatively narrow range - from about 6 to 14^{o}C. This was due to the ability of the ore mass to accumulate a portion of the heat liberated during the sulphide oxidation. However, in zones near the dump surface, where the temperature during the winter months sometimes was about 0^{o}C and even lower, the bacterial activity was temporarily ceased.

Table 5. Bacterial activity in situ at different environmental conditions

Sample tested	Fe^{2+} oxidized for 5 days, g/l	$^{14}CO_2$ fixed for 5 days, counts/min.ml (g)
Dump effluents with a pH of 2.3 + Fe^{2+} (9 g/l) at 12 – 14^{0}C	1.04 – 5.40	3 000 – 17 000
Dump effluents with a pH of 3.7 + Fe^{2+} (9 g/l) at 12 – 14^{0}C	0.77 – 3.92	2 300 – 14 000
Dump effluents with a pH of 2.3 + Fe^{2+} (9 g/l) at 6 - 8^{0}C	0.59 – 2.08	1 500 – 8 000
Dump effluents with a pH of 2.3 + Fe^{2+} (9 g/l) + $(NH_4)_2SO_4$ (1.0 g/l) + KH_2PO_4(0.2 g/l) at 12 – 14^{0}C	1.20 – 5.72	3 500 – 18 500
Ore suspensions in 9K nutrient medium (with 9 g/l Fe^{2+} and pH of 2.3) at 12 – 14^{o}C	1.27 – 6.20	3 500 – 23 000
Ore suspensions in 9K nutrient medium (with 9 g/l Fe^{2+} and pH of 2.3) at 6 – 8^{o}C	0.73 – 2.40	2 400 – 9 500

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