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Generation of Polluted Waters from Mining Wastes in a Uranium Deposit

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Abstract

Dump consisting of 9500 tons of rich-in-pyrite mining wastes located in the uranium deposit Curilo, Western Bulgaria, was, after rainfall, an intensive source of acid drainage waters. These waters had a pH in the range of about 1.7–4.5 and contained radionuclides (uranium, radium), heavy metals (copper, zinc, cadmium, lead, nickel, cobalt, iron, and manganese), arsenic and sulphates in concentrations usually much higher than the relevant permissible levels for waters intended for use in the agriculture and/or industry. The generation of these polluted waters was studied under real field conditions for a period of about seven years during different climatic seasons. It was found that the dump was inhabited by a diverse microflora in which some acidophilic chemolithotrophic bacteria were the prevalent microorganisms. The solubilization of the above-mentioned pollutants from the dump material was connected mainly with the oxidation of pyrite and other sulphide minerals by these bacteria. Their activity depended on some essential environmental factors such as temperature, pH, and water, oxygen and nutrient contents in the dump.

Key words: acid mine drainage, chemolithotrophic bacteria, bacterial oxidation of sulphide minerals, radionuclides, heavy metals

Introduction

The uranium deposit Curilo, located in Western Bulgaria, for a long period of time was site of intensive mining activities including both the open-pit and underground techniques as well as *in situ* leaching of uranium. These activities were ceased in 1990 but since that time the fractured ore body and the dumps consisting of mining wastes, after rainfall, are an intensive source of acid drainage waters. These waters have pH usually in the range of about 2–4 and contain radionuclides (uranium, radium), heavy metals (mainly iron, manganese, copper, zinc, and cadmium), arsenic and sulphates in concentrations usually much higher than the relevant permissible levels for waters intended for use in the agriculture and/or industry. The generation of such waters is connected mainly with the bacterial oxidation of pyrite and other sulphide and uranium-bearing minerals present in the mining wastes. Some data about these processes taking place in a dump consisting of rich-in-pyrite mining wastes are shown in this paper.

Experimental

Materials and Methods

The dump used as an experimental plot in this study was formed on a moderately steep hill without any ground preparation. The dump consisted of run-of-mine mining wastes and included different particle sizes – from very fine (less than 100 microns) to boulders as large as 0.1–0.3 m in diameter. The dump contained about 9 500 tons of mining wastes.

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 mining wastes were nasturane, torbernite, metatorbernite, pitch-blende, metaotunate and basetite. Quartz was the main mineral of the host rock. Clay minerals and some iron hydroxides were also present in the dump.

The quality of the dump effluents was monitored at least once per month in the period April 1997 – November 2003. The parameters measured *in situ* included pH, Eh, dissolved oxygen, total dissolved solids and temperature. Elemental analysis

Table I
Data about the chemical composition and some geotechnical parameters of the dump material

Parameters	Value	Parameters	Value
Chemical composition:		Pb, g/t	521
SiO_2, %	68.0	Ni, g/t	104
Fe_2O_3, %	5.94	Co, g/t	82
Al_2O_3, %	5.67	Mn, g/t	648
CaO, %	0.37	As, g/t	99
MgO, %	0.23	pH (H_2O)	2.77
S total, %	2.31	Net neutralization potential, kg $CaCO_3$/t	– 245
S sulphidic, %	1.70	Bulk density, g/m^3	1.69
U, g/t	170	Specific density, g/m^3	2.82
Cu, g/t	1045	Porosity, %	44
Zn, g/t	710	Permeability, m/s	8×10^{-2}
Cd, g/t	28		

was done by atomic absorption spectrometry and induced coupled plasma spectrometry 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 ^{226}Ra was measured using a 10 l ionization chamber.

The procedures for collecting liquid or solid samples for microbiological analysis and the procedure for isolation, identification and enumeration of different microorganisms have been described earlier (Karavaiko *et al.*, 1988; Groudeva *et al.*, 1993). Phylogenetic analyses based on 16S r RNA gene sequence was performed for speciation of the prevalent isolates from the dumps (Hallberg and Johnson, 2001). 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 by the shake-flask technique and in percolation columns. Data about the chemical composition and some essential geotechnical parameters of this sample are shown in Table I. The leaching by the shake-flask technique was carried out in 2 l Erlenmeyer flasks containing 450 ml iron-free 9K nutrient medium (Silverman and Lundgren, 1959), 200 g dump material crushed to minus 400 mesh and 50 ml of an active late-log phase mixed or pure culture of chemolithotrophic bacteria preliminarily adapted to the material being leached and containing about 5×10^8 cells/ml. The column leaching was carried out in PVC percolation columns with an effective length of 550 mm and a 200 mm internal diameter. Each column was charged with 10 kg of fresh ore used within 24 after its collection from the dump. The ore contained viable microflora and was crushed to less than 10 mm in size. 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 experiments the pregnant column effluents were recycled to the tops of the columns and were circulated in this way allowing pollutants to accumulate. In some other experiments the pregnant column effluents were removed from the system after a single passage through the mining wastes.

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 inoculated with freshly collected samples of mining wastes. These experiments were carried out in 300 ml Erlenmeyer flasks containing 100 ml liquid phase. The flasks were incubated *in situ* at 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 modifications (Groudev and Groudeva 1993) to determine the $^{14}CO_2$ fixation *in situ.*

Results and Discussion

The dump used in this study was after rainfall an intensive source of acid drainage waters (Table II). Their flow rate dependent mainly on the level of rainfall and the ambient temperature and during the period of study varied in the range of about 0–0.5 l/s. The generation of these waters was connected with the oxidative activity of the acidophilic chemolithotrophic bacteria which inhabited the dump (Tables III and IV). *Acidithiobacillus ferrooxidans, Leptospirillum ferrooxidans* and *Acidithiobacillus thiooxidans* were the prevalent species in this microbial community. Moderately thermophilic chemolithotrophic bacteria, mainly such related to the species *Sulfobacillus thermosulfidooxidans* and *Acidithiobacillus caldus*, were found in some rich-in-pyrite dump sections, in which the temperature during the warmer months of the year exceeded 45°C. Some thermotolerant members of the genus *Leptospirillum* were also found in these sections. Extremely thermophilic chemolithotrophic bacteria, including such related to the genera *Sulfolobus* and *Acidianus,* were not detected in the dump and in the dump effluents. Some heterotrophic bacteria (mainly such related to the genus *Acidiphilium*) were also typical members of the acidophilic microbial community

Table II
Data about the dump effluents

Parameters	Values	Permissible levels for waters used in agriculture and industry
Temperature, °C	(+ 4.8) – (+ 14.3)	–
pH	1.70 – 4.46	6–9
Eh, mV	(+ 378) – (+ 602)	–
Dissolved oxygen, mg/l	1.7 – 4.4	2
Total dissolved solids, mg/l	701 – 2462	1500
Solids, mg/l	35 – 145	100
Sulphates, mg/l	374 – 1375	400
Uranium, mg/l	0.32 – 4.04	0.6
Radium, Bq/l	0.10 – 0.35	0.15
Copper, mg/l	0.71 – 10.04	0.5
Zinc, mg/l	1.25 – 19.40	10
Cadmium, mg/l	0.02 – 0.10	0.02
Lead, mg/l	0.14 – 0.59	0.2
Nickel, mg/l	0.32 – 1.40	0.5
Cobalt, mg/l	0.23 – 1.22	0.5
Iron, mg/l	132 – 802	5
Manganese, mg/l	0.9 – 17.2	0.8
Arsenic, mg/l	0.05 – 0.32	0.2

Table III
Microorganisms in the dump and in the dump effluents

Microorganisms	In the dump		In the dump effluents	
	At depths 0–3 m	At depths >4 m	During the warmer months	During the cold (0–5°C) periods
	Cells/g		Cells/ml	
Fe^{2+} – oxidizing chemolithotrophs (at pH 2)	$10^5 – 10^9$	$10^1 – 10^5$	$10^4 – 10^8$	$10^2 – 10^5$
S° – oxidizing chemolithotrophs (at pH 2)	$10^4 – 10^8$	$10^1 – 10^5$	$10^4 – 10^8$	$10^1 – 10^5$
Aerobic heterotrophic bacteria (at pH 2)	$10^1 – 10^4$	$0 – 10^2$	$10^1 – 10^2$	$0 – 10^2$
$S_2O_3^{2-}$ – oxidizing chemolithotrophs (at pH 7)	$0 – 10^3$	$0 – 10^2$	$0 – 10^2$	$0 – 10^2$
Aerobic heterotrophic bacteria (at pH 7)	$0 – 10^2$	$0 – 10^1$	$0 – 10^1$	$0 – 10^1$
Anaerobic heterotrophic bacteria (at pH 7)	$0 – 10^1$	$0 – 10^4$	$0 – 10^1$	$0 – 10^1$
Sulfate-reducing bacteria	$0 – 10^2$	$0 – 10^4$	$0 – 10^2$	$0 – 10^1$
Denitrifying bacteria	$0 – 10^2$	$0 – 10^2$	$0 – 10^1$	$0 – 10^1$
Fe^{3+} – reducing bacteria	$0 – 10^1$	$0 – 10^3$	$0 – 10^1$	$0 – 10^1$
Methanogenic bacteria	ND	$0 – 10^2$	ND	ND
Fungi	$0 – 10^2$	$0 – 10^1$	$0 – 10^1$	ND

Note: ND – not detected

which inhabited the aerobic zone in the dump. This zone reached depths of about 3–4 m from the surface. The distribution of the chemolithotrophic bacteria in this zone was not homogenous and their density varied in the range of about 10^4–10^8 cells/g dump material. The number of chemolithotrophs decreased with increasing depth and in the anaerobic zone was negligible. The presence of such bacteria in the deeply located dump layers was connected with their transport by the drainage waters which usually still contained some dissolved oxygen.

Sulphate-reducing bacteria as well as bacteria able to reduce the Fe^{3+} and Mn^{4+} were the main inhabitant of the anaerobic zone. However, the density of these heterotrophs was low due to the shortage of organic

Table IV
Bacterial activity *in situ* under 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 1.7–2.5 + Fe^{2+} (9 g/l) at 12–14°C	1.18 – 6.11	2800 – 16700
Dump effluents with a pH of 3.2–3.7 + Fe^{2+} (9 g/l) at 12–14°C	0.82 – 4.46	2300 – 12900
Dump effluents with a pH of 1.7–2.5 + Fe^{2+} (9 g/l) at 5–7°C	0.51 – 1.85	1400 – 5900
Dump effluents with a pH of 1.7–2.5 + Fe^{2+} (9 g/l) + $(NH_4)_2SO_4$ (1.0 g/l) + KH_2PO_4 (0.5 g/l) at 12–14°C	1.61 – 6.75	4500 – 19400
Ore suspensions in 9K nutrient medium (with 9 g/l Fe^{2+} and pH 2.3) at 12–14°C	1.50 – 7.07	4400 – 20800
Ore suspensions in 9K nutrient medium (with 9 g/l Fe^{2+} and pH 2.3) at 5–7°C	0.48 – 2.75	1400 – 7300

Table V
Bacterial leaching of dump material by the shake-flask techniques at different temperatures

Microorganisms	Metal solubilized within 20 days, %				
	U	Cu	Zn	Fe	Mn
Mixed mesophilic culture at 15°C	23.9	10.7	22.4	3.2	23.5
Mixed mesophilic culture at 35°C	48.2	19.4	46.0	5.9	47.1
Mixed thermophilic culture at 50°C	59.4	25.7	57.8	8.2	58.5
A. ferrooxidans at 15°C	19.0	8.6	20.1	3.0	21.5
L. ferrooxidans at 15°C	9.5	3.7	9.9	3.0	4.1
S. thermosulfidooxidans at 50°C	51.8	19.8	47.7	6.2	50.5
Chemical leaching at:					
15°C	3.2	1.7	3.5	0.5	3.5
35°C	6.4	3.5	7.3	0.9	7.0
50°C	11.8	7.0	12.9	1.8	12.5

donors of electrons. For that reason, the process of microbial dissimilatory sulphate reduction was limited and had not a significant effect on the acidity and the contents of sulphates, uranium and heavy metals in the drainage waters passing through this zone. Regardless of this, the amount of secondary sulphides of iron, non-ferrous metals and arsenic as well as of precipitates containing insoluble tetravalent uranium was considerably increased in comparison with that in typical freshly excavated samples of low-grade ores, *i.e.* mining wastes, from the deposit.

The leaching experiment by means of the shake-flask technique revealed that the mixed cultures of both mesophilic and moderately chemolithotrophic bacteria leached pollutants from the mining wastes more efficiently than the pure cultures consisting of the prevalent microorganism in the relevant mixed culture (Table V). This is an indication that the different members of the mixed culture exert a synergetic effect during the leaching.

The results from the column leaching experiments confirmed that the indigenous chemolithotrophic bacteria were able to leach efficiently pollutants from the dump material and to produce drainage waters with composition similar to that of the drainage waters generated under natural conditions. The microbial activity *in situ* depended on some essential environmental factors such as the water and oxygen content in the dump material, pH and composition of the waters penetrating through this material as well as the level of the ambient temperature. The highest activity was measured in zones with a pH in the range of about 1.7–2.5. In zones with pH higher than 3.5 both the number and activity of the acidophilic chemolithotrophs were relatively low. Water content higher than 45–50% was needed for optimal bacterial activity. However, in zones consisting of mining wastes saturated with water (after heavy rainfall) the activity was lower and this was connected not only with the dilution effect increasing the local pH to levels higher than 3.5 but also with the shortage of oxygen due to its low solubility in water. The highest bacterial activity was measured in the upper layers of the dump when the mineral particles were covered by thin water films facilitating the natural aeration. The addition of ammonium and phosphate ions to the dump had only a slight positive effect on the number and activity of the acidophilic chemolithotrophs. This was due to the fact that the natural concentrations of these ions, although relatively low (less than 10 mg/l for each of these ions), were sufficient to maintain the bacterial growth and activity under the real dump conditions. The temperature inside the real dump varied during the different climatic seasons within a relatively narrow range – from about 5 to 14°C. This was due to the ability of the mineral mass to accumulate a portion of the heat liberated during the sulphide oxidation. However, in the zones near the dump surface, where the temperature during the cold winter months was about 0°C or even lower, the bacterial activity was temporarily ceased.

The data obtained during this study can be used as a base of technologies for preventing the generation of acid drainage by inhibition of the indigenous acidophilic chemolithotrophic bacteria as a result of suitable changes in the levels of some of the above-mentioned essential environmental factors.

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