PREVENTION OF THE GENERATION OF ACID DRAINAGE WATERS IN A HEAP CONSISTING OF URANIUM-BEARING MINING WASTES

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ABSTRACT. The generation of heavily polluted acid mine drainages was an essential environmental problem in most of the Bulgarian uranium deposits after the end of their industrial scale development. Different methods to prevent this generation were tested and one of the most efficient of them is present in this paper. An experimental heap consisting of about 550 tons of rich-in-pyrite mining wastes located in the uranium deposit Curilo was a site, after rainfall, of generation of drainage waters with a pH in the range of about 1.5 – 3.5 and polluted by radionuclides, heavy metals, arsenic and sulphates. The generation was connected with the presence of numerous populations of acidophilic chemolithotrophic bacteria which oxidized the pyrite, the other sulphides and uranium present in the heap and the products of the relevant oxidation reactions solubilized in the drainage waters. The inhibition of this process was achieved by the construction of an about 40 – 45 cm layer consisting of a mixture of soil, solid biodegradable organic substrates (plant compost, animal manure, straw) and crushed limestone to form a heap cover with a slightly alkaline pH (about 7.5 – 8). Some herbaceous plants were sowed in this cover. This new ecosystem was inhabited by a microbial community consisting mainly of different heterotrophic microorganisms and by periodic addition of limestone was made not suitable for acidophilic chemolithotrophic bacteria.

Key words: Acid drainage, Uranium, Mining wastes

ПРЕДОТВРАТЯВАНЕ НА ГЕНЕРИРАНЕТО НА КИСЕЛИ ДРЕНАЖНИ ВОДИ В ХАЛДА, СЪСТОЯЩА СЕ ОТ УРАН-СЪДЪРЖАЩИ МИННИ ОТПАДЪЦИ

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РЕЗЮМЕ. Генерирането на тежко замърсени кисели руднични дренажни води беше съществен екологичен проблем в повечето от българските уранови находища след прекратяването на тяхното промишлено разработване. Различни методи за да се предотврати това генериране бяха тестирани и най-ефикасният от тях е представен в тази публикация. Експериментална халда, състояща се от около 550 тона богати на пирит минни отпадъци, разположена в урановото находище Курило, беше след дъждове обект за генериране на дренажни води с pH в областта около 1.5 – 3.5 и замърсени с радионуклиди, тежки метали, арсен и сулфати. Генерирането беше свързано с присъстваието на многочислени популации на ацидофилни хемолитотрофни бактерии, които окисляваха пирита, другите сулфиди и урана в халдата, както и някои от разтворените в дренажните води продукти от съответните окислителни реакции. Инхибирането на този процес беше постигнато чрез конструирането на около 40 – 45 cm пласт, състоящ се от смес на почва, твърди биологично разградими органични субстрати (растителен компост, животински тор, слама) и натрошен варовик, за да се образува върху халдата покривен пласт със слабо алкално pH (около 7.5 – 8). Някои тревисти растения бяха насадени в този покривен пласт. Тази нова екосистема беше обитавана от микробно съобщество, състояща се главно от различни хетеротрофни микроорганизми, като чрез периодично внасяне на варовик този пласт беше поддържан неподходящ за ацидофилните хемолитотрофни бактерии.

Ключови думи: Кисели дренажни води, Уран, Минни отпадъци

Introduction

The uranium deposit Curilo, located in a short distance from the capital city Sofia, for a long period of time was a site of intensive mining activities including both open-pit and underground techniques as well as in situ leaching of uranium. The mining operations were ended in 1990 but until recently both the surface and ground waters and soils within and near the deposit were heavily contaminated with radionuclides (mainly uranium and radium) and toxic heavy metals (mainly copper and zinc but also cadmium, lead, nickel, cobalt, molybdenum, iron) and arsenic. The main sources of these contaminants were some dumps and heaps consisting of mining wastes which only few years ago were subjected to an efficient recultivation. These dumps and heaps were inhabited by different chemolithotrophic bacteria which oxidized the pyrite, sulphide minerals and the tetravalent uranium present in the mining waters, generating in this way acid drainage waters containing the contaminants above-mentioned in soluble forms (most of them mainly as the relevant sulphates but lead as complexes with some organic acids).

Different methods to prevent and/or inhibit this generation were tested and one of the most efficient of them is present in this paper.

Materials and Methods

An experimental heap consisting of about 550 tons of rich-in-pyrite mining wastes located in the Curilo deposit was a site, after rainfall, of generation of drainage waters with a pH in the range of about 1.5 – 3.5 and polluted by radionuclides, heavy metals, arsenic and sulphates.

Data about the chemical composition of the mining wastes and their essential geotechnical parameters are shown in Tables 1 and 2, respectively. Pyrite was the main ore mineral. Uranium was present mainly as uraninite, nasturan, torbernite. Chalcopyrite was the main copper-bearing mineral but some secondary copper sulphides such as covellite and chalcocite were also present, together with some copper oxide minerals. Zinc was present mainly as sphalerite, and lead mainly as galena. Arsenopyrite was the main arsenic-bearing mineral. Quartz was the main mineral of the host rock.

Table 1.
Data about the chemical composition of the mining wastes

Component	Content	Component	Content
SiO_2	68.6 %	Cu	815 g/t
Al_2O_3	5.94 %	Zn	541 g/t
CaO	0.35 %	Cd	28 g/t
MgO	0.18 %	Pb	419 g/t
S total	1.61 %	Ni	102 g/t
S sulphidic	1.16 %	Co	88 g/t
Fe	3. 98 %	Mo	51 g/t
U	149 g/t	Mn	591 g/t
Ra	122 Bq/kg	As	104 g/t

Table 2.
Essential geotechnical parameters of the mining wastes

Parameters	Value
$pH(H_2O)$	2.75
Bulk density, g/cm^2	1.69
Specific density, g/cm^2	2.81
Net neutralization potential, kg $CaCO_3$/t	-23
Porosity, %	44
Permeability, cm/h	32

The elemental analysis of the heap effluents was done by atomic adsorption spectrometry and induced coupled plasma spectrometry. Sulphate was determined photometrically. The radioactivity of the samples was measured, using the solid residues remaining after their evaporation, by means of a low background gamma-spectrometer ORTEC (HpGe-detector with a high distinguishing ability).

The main geotechnical characteristics of the heap, such as permeability and wet bulk density, were measured in situ using sand-core method (U.S. Environmental Protection Agency, 1991). True density measurements were carried out in the laboratory using undisturbed core samples. Such samples were also used for determination of their acid generation and net neutralization potentials using static acid-base accounting tests.

The isolation, identification and enumeration of the microorganisms were carried out by methods described elsewhere (Karavaiko et al., 1988; Johnson and Hallberg, 2003; Escobar et al., 2008).

The inhibition of the generation of acid drainage waters was achieved by means of construction of an about 40 – 45 cm cover on the mining wastes. A mixture of a slightly leached cinnamonic forest soil (which is typical for this region), with some solid biodegradable organic substrates (plant compost, animal manure, straw) and crushed limestone, was used to form this heap cover with a slightly alkaline pH (about 7.5 – 8).

The main component of the heap cover, i.e. the slightly leached cinnamonic forest soil, had pH of 6.8 (in H_2O) and contained 1.90 % humus, 78.1 % SiO_2, 2.35 % Fe_2O_3, 0.10 % total nitrogen, 2.21 % K_2O, 0.15 % P_2O_5 as the essential components. The soil contained viable microflora which practically was the main source of microorganisms in the constructed cover on the mining wastes. The fertility of the soil cover was enhanced by adding compost to the soil at amounts of 10 – 20 % on dry weight.

The preparation of the compost, i.e. the procedure of composting, was carried out with a mixture consisting of plant (leaf) biomass, animal manure, cinnamonic forest soil and a biofertilzier obtained by processing of activated sludge from the system for municipal wastewater treatment (Nicolova et al., 2012). The components were mixed in a ratio of 7:1:1:1 on dry weight.

The batches of compost produced in this way had pH of about 6.8 – 7.1 and contained 50 – 55 % dry substances, with 40 – 45 % ash content and 55 – 60 % organic content (with 40 – 45 % organic carbon and nitrogen content of 2.0 – 2.5 % at a ratio of C:N of about 20 (all these contents are on dry weight). The moisture of the different batches of compost was about 45 – 50 %.

The heap cover contained some non-ferrous metals (Cu, Zn, Pb, Ni, Co) but each of them in concentrations lower than 50 mg/kg on dry weight)

Results and Discussion

The generation of acid drainage waters in the heap before its recultivation was connected with the activity of the indigenous microorganisms, mainly of the acidophilic chemolithotrophic bacteria, which oxidize the pyrite and other sulphide minerals producing in situ diluted solutions of sulphuric acid containing dissolved heavy metals, uranium and arsenic as the main toxic pollutants. Radium was only slightly soluble in these highly acidic solutions, mainly in the form of complexes with some organic compounds.

The mesophilic chemolithotrophic bacteria *At. ferrooxidans* and *L. ferrooxidans* were the main species participating in these oxidation processes but some moderate thermophiles (mainly *Sulfobacillus thermosufidooxidans*) were also involved, although in lower extent (Table 3).

Table 3.
Microflora composition of the heap consisting of mining wastes

Microorganisms	Cells/g dry sample
Acidithiobacillus ferrooxidans	$10^5 – 10^8$
Acidithiobacillus thiooxidans	$10^2 – 10^6$
Leptospirillum ferrooxidans	$10^4 – 10^8$
Moderately thermophilic chemolithotrophic bacteria (*Thiobacillus caldus, Sulfobacillus thermosulfidooxidans*)	$0 – 10^4$
Extremely thermophilic archaea (*Sulfolobus, Acidianus*)	0
Chemolithotrophic bacteria growing at neutral and alkaline pH (*Thiobacillus thioparus, T. neapolitanus, T. novellus, T. denitrificans*)	$10^1 – 10^3$
Heterotrophic bacteria	$0 – 10^3$
Fungi	$0 – 10^2$

The soil cover constructed on the mining wastes was a completely different ecosystem enriched in biodegradable organic substances, with a neutral pH (in the range of 6.8 – 7.1) and practically free of radionuclides and dissolved heavy metals and arsenic (Table 4). This cover had a microflora composition typical for the rich-in-organic fat lands (Table 5). The content of chemolithotrophic bacteria in this cover was quite low and consisted of species able to grow at pH values close to the neutral point. Some herbaceous plants grew well on the cover.

Table 4.
Chemical composition of the soil cover formed on the heap consisting of mining wastes

Parameters	Values
pH (H_2O)	6.8 – 7.1
Organic substance (including humus)	3.8 – 4.7 %
Total nitrogen	0.23 %
SiO_2	76.1 %
Al_2O_3	12.2 %
Fe_2O_3	2.01 %
P_2O_5	0.11 %
K_2O	1.61 %
CaO	0.54 %
MgO	0.37 %

Table 5.
Microflora composition of the soil cover formed on the heap consisting of mining wastes

Microorganisms	Cells/g dry soil
Aerobic heterotrophic bacteria	$3.10^8 – 8.10^8$
Cellulose-degrading bacteria	$3.10^6 – 2.10^7$
Nitrifying bacteria	$9.10^5 – 6.10^6$
"Silicate" bacteria	$5.10^5 – 4.10^6$
Ammonifying bacteria	$6.10^6 – 8.10^7$
Nitrogen-fixing bacteria	$9.10^4 – 7.10^6$
Anaerobic heterotrophic bacteria	$6.10^4 – 1.10^6$
Fungi	$7.10^5 – 2.10^7$
Chemolithotrophic S-oxidizing bacteria	$4.10^1 – 2.10^4$

The construction of the soil cover deeply changed the environmental conditions in the mining wastes located below this cover. The former heap of mining wastes changed into a mainly anaerobic ecosystem, with a neutral pH, i.e. a system unfavourable for the growth and activity of the acidophilic, mainly aerobic, chemolithotrophic bacteria. The former typical mineral ecosystem gradually was enriched in organic compounds transported from the soil cover by the drainage waters. This new anaerobic system containing biodegradable organic substrates at almost neutral pH was inhabited mainly by different sulphate-reducing bacteria. The metabolism of these bacteria was connected with the process of the microbial dissimilatory sulphate reduction, which generated hydrogen sulphide (H_2S) as an essential product. The hydrogen sulphide precipitated efficiently as the relevant sulphide each heavy metal penetrated into this anaerobic zone by the drainage waters from the top soil cover. The soluble hexavalent uranium was reduced and precipitated as the insoluble tetravalent form. As a result of these deep changes, the effluents from the heap of mining wastes after rains were with a composition completely acceptable with respect to the current environmental standards (Table 6).

Table 6.
Chemical composition of the heap effluents before and after the recultivation of the heap

Parameters	Before treatment	After recultivation	Permissible levels
pH	1.54 – 3.52	6.5 – 7.1	6 – 9
Diss. O_2, mg/l	1.9 – 4.4	1.4 – 2.3	2
TDS, mg/l	842 – 2394	745 – 1250	1500
Solids, mg/l	41 – 125	37 – 95	100
Diss. C_{org}, mg/l	0.3 – 0.9	21 – 46	–
Sulphates, mg/l	451 – 1465	280 – 415	400
U, mg/l	0.32 – 3.74	0.21 – 0.51	0.6
Ra, Bq/l	0.05 – 0.37	< 0.10	0.15
Cu, mg/l	0.77 – 7.12	< 0.5	0.5
Zn, mg/l	1.22 – 15.4	0.3 – 1.4	10
Cd, mg/l	0.02 – 0.10	< 0.02	0.02
Pb, mg/l	0.15 – 0.64	< 0.10	0.2
Ni, mg/l	0.32 – 1.20	0.08 – 0.28	0.5
Co, mg/l	0.25 – 1.07	0.10 – 0.23	0.5
Fe, mg/l	152 – 1252	4 – 31	5
Mn, mg/l	0.9 – 14.6	0.3 – 0.8	0.8
As, mg/l	0.05 – 0.37	< 0.10	0.1

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