CLEANUP OF ACID MINE DRAINAGE BY MEANS OF A PILOT-SCALE PASSIVE SYSTEM

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ABSTRACT. Acid mine drainage with a pH in the range of about 2.5-4 and containing radionuclides (mainly uranium and radium), heavy metals (copper, zinc, cadmium, lead, nickel, cobalt, iron, manganese), arsenic and sulphates as main pollutants were treated by means of a pilot-scale passive system consisting of an alkalizing limestone drain, a permeable reactive barrier for microbial sulphate reduction and biosorption, and a natural wetland, connected in a series. An efficient removal of the pollutants was achieved by this system, even during the cold winter months at temperatures close to 0 °C. Iron was removed mainly as hydroxides in the alkalizing drain and as sulphide in the permeable barrier. Uranium, non-ferrous metals and arsenic were removed mainly in the barrier as a result of the activity of the indigenous sulphate-reducing bacteria. Manganese was removed mainly as MnO₂ after the prior bacterial oxidation of the Mn²* ions to the tetravalent state. Portions of all these pollutants were removed and by sorption on the dead plant biomass present in the barrier.

ПРЕЧИСТВАНЕ НА КИСЕЛИ РУДНИЧНИ ВОДИ ПОСРЕДСТВОМ ПИЛОТНА ПАСИВНА СИСТЕМА

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РЕЗЮМЕ. Кисели руднични води с pH в областта около 2.5-4 и съдържащи радионуклиди (главно уран и радий), тежки метали (мед, цинк, кадмий, никел, кобалт, желязо, манган), арсен и сулфати като главни замърсители, бяха третирани посредством пасивна система, състояща се от алкализиращ варовиков дренаж, пропусклива реактивна бариера за микробна дисимилативна сулфатредукция и биосорбция, и естествено мочурище, свързани последователно. Посредством тази система бе постигнато ефикасно отстраняване на замърсителите, дори през студените зимни месеци, при температури близки до 0 °С. Желязото бе отстранено главно като хидроокиси в алкализиращи дренаж и като сулфид в пропускливата бариера. Уранът, цветните метали и арсена бяха отстранени главно в бариерата в резултат на активността на обитаващите я сулфат редуциращи бактерии. Мангана бе отстранен главно като MnO₂ след предварителното бактериално окисление на Mn²⁺ йони до четиривалентната форма. Част от всички тези замърсители бяха отстранени и чрез сорбция вързу мъртвата растителна биомаса в бариерата.

Introduction

The acid mine drainage waters generated in the uranium deposit Curilo, Western Bulgaria, are a heavy environmental problem, especially after the end of the mining operations fifteen years ago. The fractured ore body and the several dumps consisting of mining wastes are, especially after rainfall, the main sources of these waters. The waters have a low pH (usually in the range of 2.5-4.0) and contain heavy metals, radionuclides, arsenic and sulphates in concentrations usually much higher than the relevant permissible levels for waters intended for use in agriculture and/or industry. The solubilization of these pollutants from the residual ore in the deposit is connected mainly with the oxidative activity of the indigenous acidophilic chemolithotrophic bacteria (Groudev et al., 2003).

Different methods to cleanup the above-mentioned polluted waters were tested under laboratory and pilot-scale conditions. Most of these methods were connected with the application of various passive systems such as alkalizing drains, natural and constructed wetlands, permeable reactive barriers and rock filters, used separately or in different combinations (Groudev et al., 2002, 2003a, 2003b, 2003c, 2004). Some data about

treatment of such waters by means of a passive system consisting of an alkalizing limestone drain, an anoxic barrier for microbial dissimilatory sulphates reduction and biosorption and a natural wetland, connected in a series, are presented in this paper.

Materials and methods

The passive system was constructed in a ravine collecting a portion of the acid drainage waters generated in the deposit. The alkalizing limestone drain was a pond with a volume of about 2.5 m³ (1.0 m long, 1.7 m wide and 1.5 m deep). The pond was constructed by using acid-resistant concrete and was filled with a mixture of crushed limestone and gravel (in a ratio of about 1:2 as dry weight) with a particle size less than 12 mm. The surface of this mixture was covered by a permeable textile cover intended to retain the solid particles, consisting mainly of iron and aluminum hydroxides, suspended in the drain effluents. Another cover of the same material was located in the drain, at a depth of 10 cm from the surface, to separate the top limestone-gravel layer in which some oxygen was present, from deeply located mass of these materials. This second cover retained the iron hydroxides generated in the

upper layer and prevented their seepage into the deeply located material. The permeable barrier had a volume of about 20.4 m^3 (8.0 m long, 1.7 m wide, and 1.5 m deep) and was filled by a mixture of biodegradable solid organic substrates (cow manure, plant compost, straw), crushed limestone an zeolite saturated with ammonium phosphate. The barrier was inhabited by a microbial community consisting mainly of bacteria and other sulphates-reducing metabolically interdependent microorganisms (Table 1). The natural wetland covered an area of about 80 m² and was characterized by an abundant water and emergent vegetation and a diverse microflora. Typha latifolia and Typha angustifolia were the main plant species in the wetland but species related to the genera Juncus, Eleocharis, Phragmites, Potamogeton, Carex and Poa as well as different algae were also present. The passive system was put into operation in the beginning of July 2004. Until now (May 2005), the water flow rate through the passive system was maintained in the range of about 1-10 m³/24 h, with a tendency for a gradual increase.

Table 1

Microorganisms in the acid mine drainage and in effluents from the permeable reactive barrier

Microorganisms	In the	In the
	acid	barrier
	mine	effluents
	drainage	
	Cells/ml	
Fe ²⁺ -oxidizing chemolithotrophs (at pH 2)	10 ⁴ - 10 ⁷	0 – 10 ²
Aerobic heterotrophs (at pH 2)	10 ¹ – 10 ⁴	0 – 10 ¹
S ₂ O ₃ ² -oxidizing chemolithotrophs (at pH 7)	0 – 10 ³	10 ² – 10 ³
Aerobic heterotrophs (at pH 7)	0 – 10 ²	10 ¹ – 10 ⁴
Anaerobic heterotrophs (at pH 7)	0 –10 ¹	10 ⁴ – 10 ⁷
Sulphate-reducing bacteria	0 – 10 ¹	10 ⁴ – 10 ⁷
Cellulose-degrading microorganisms	ND	10 ³ – 10 ⁶
Bacteria fermenting sugars with gas production	ND	10 ⁴ – 10 ⁷
Ammonifying bacteria	ND	10 ² – 10 ⁵
Denitrifying bacteria	ND	10 ² – 10 ⁵
Fe ³⁺ -reducing bacteria	ND	10 ³ – 10 ⁶
Methane-producing bacteria	ND	10 ¹ – 10 ⁵

Note: ND = not detected

The quality of the waters was monitored at different sampling points located at the inlet and the outlet of the abovementioned three units of the treatment system, as well as at different sites in the permeable barrier. Elemental analysis was done by atomic adsorption spectrophotometry and induced coupled plasma spectrophotometry. The radioactivity of the samples was measured, using the solid residues remaining after their evaporation, by means of a low background gamma-spectrophotometers ORTEC (HpGe – detector with a high distinguishing ability). The specific activity of ²²⁶Ra was measured using 10 l ionization chamber.

Mineralogical analysis was carried out by X-ray diffraction techniques. The mobility of the pollutants was determined by the sequential extraction procedure (Tessier et al., 1979). The isolation, identification and enumeration of microorganisms were carried out by methods described elsewhere (Karavaiko

et al., 1988; Widdel and Hansen, 1991; Widdel and Bak, 1991; Groudeva and Tzeneva, 2001).

Results and discussions

An efficient cleanup of the acid mine drainage was achieved by the passive treatment system. The essential removal of pollutants was performed in the alkalizing drain and in the permeable reactive barrier (Table 2), at total residence times in the range of about 300 to 30 hours. In the alkalizing drain the pH of the waters was increased to values around the neutral point and as a result of this most of the iron (present as Fe³⁺ ions) was precipitated as ferric hydroxides. Portions of the nonferric metals and aluminium (usually from 20 to 50 %) were also removed in the drain as a result of hydrolysis and subsequent precipitation as the relevant hydroxides. A portion of arsenic was also removed, mainly by means of sorption on the iron hydroxides.

Table 2

Composition of the acid mine drainage and of the effluents	i
from the permeable reactive barrier	

		-	
Parameters	Acid mine	Barrier	Permissible
	drainage	effluents	levels for
			waters
			intended for
			use in
			agriculture
			and industry
Temperature, °C	(+1.2)-(+24.0)	(+1.2)-(+25.9)	-
pН	2.42 – 4.15	6.22 – 7.74	6 – 9
Eh, mV	(+350)-(+597)	(-140)-(-280)	-
Dissolved O2, mg/l	1.7 – 5.9	0.2 – 0.4	2
TDS, mg/l	930 – 2972	545 – 1827	1500
Solids, mg/l	41 – 159	32 – 104	100
DOC, mg/l	0.5 – 2.1	59 – 152	20
SO4 ²⁻ , mg/l	532 – 2057	275 – 1225	400
U, mg/l	0.10 – 2.51	< 0.05	0.6
Ra, Bq/I	0.05 – 0.50	< 0.03	0.15
Cu, mg/l	0.79 – 8.24	< 0.20	0.5
Zn, mg/l	0.59 – 14.90	< 0.20	10
Cd, mg/l	<0.01 – 0.10	< 0.004	0.02
Pb, mg/l	0.08 – 0.55	< 0.02	0.2
Ni, mg/l	0.23 – 1.45	< 0.03 – 0.10	0.5
Co, mg/l	0.15 – 1.04	< 0.03 – 0.10	0.5
Fe, mg/l	41 – 640	0.7 – 9.1	5
Mn, mg/l	3.2 – 27.1	0.7 – 4.8	0.8
As, mg/l	0.05 – 0.32	< 0.01	0.2

The removal of the residual concentrations of pollutants in the permeable barrier was connected with different biological, chemical and physico-chemical process but the microbial dissimilatory sulphates reduction and the sorption of pollutants by the dead solid plant biomass played the main role. The anaerobic sulphate-reducing bacteria were a quite numerous and diverse population in the barrier. The dominant and the most active strains were related of the genera *Desulfovibrio* (mainly *D. desulfuricans*) and *Desulfobulbus* (mainly *D. elongatus*) but representatives of the genera *Desulfococcus*, *Desulfobacter* and *Desulfosarcina* were also well present. As a result of their activity the pH of the waters was stabilized around the neutral point due to the generation of hydrocarbonate ions during the microbial sulphate reduction. The residual concentrations of non-ferrous metals, iron and arsenic were precipitated mainly as the relevant insoluble sulphides. Uranium was precipitated mainly as uraninite (UO₂) as a result of the prior reduction of the hexavalent uranium to the tetravalent form. However, portions of these pollutants as well as most of the radium were removed by sorption on the dead plant biomass (Table 3). Only small amounts of the pollutants were precipitates as the relevant hydroxides or carbonates. Apart from the chemical and mineralogical analyses of the sediments in the barrier, the above findings were established also by the data from the subsequent extraction procedure (Table 4).

Table 3

Content of pollutants in the dead solid plant biomass in the permeable reactive barrier

Pollutants	Content, mg/kg dry biomass
Uranium	10 – 73
Radium	5 – 35
Copper	32 – 170
Zinc	14 – 71
Cadmium	2 – 21
Lead	9 – 55
Nickel	10 – 68
Cobalt	10 – 59
Manganese	37 – 172
Arsenic	4 – 24

Table 4

Distribution of pollutants in sediments from the permeable reactive barrier into different mobility fractions (as % from the total content of the respective pollutant)

Pollutants	ints Portions of pollutants in different mobility fractions, %			
-	Exchangeable	Carbonate	Oxidizable	Reducible
U	7 – 44	3 – 12	62 – 88	2 – 6
Ra	71 – 88	3 – 11	2 – 7	4 – 14
Cu	8 – 35	4 – 16	60 – 82	4 – 8
Mn	6 – 25	5 – 15	2 – 6	64 – 88
Fe	7 – 18	5 – 16	65 – 86	2 – 10

The effluents from the barrier were enriched in dissolved organic compounds and usually still contained manganese in concentrations higher than the relevant permissible levels (Table 2). These effluents were treated in the natural wetland where the Mn^{2+} ions were oxidized to Mn^{4+} by some heterotrophic bacteria producing peroxide compounds and the enzyme catalase, which degraded the excess to peroxides to molecular oxygen and water. The Mn^{4+} ions precipitated as MnO_2 . The dissolved organic compounds were degraded by the different heterotrophs inhabiting the wetland.

The water cleanup markedly depended on the temperature but was efficient even during the cold winter months at ambient temperatures close to 0°C (Table 5), although at longer residence times. During these cold months, when the growth and activity of the microbial community in the permeable barrier were considerably inhabited, the role played by the solid dead plant biomass as a sorbent of pollutants was essential.

Table 5

Removal of pollutants from the acid mine drainage by means of the passive treatment system during different climatic seasons

Pollutants	Pollutants removed, g/24 h		
	During the	During the cold winter	
	warmer months	months (at 0-5 °C)	
Uranium	2.42 – 17.2	0.35 – 2.27	
Copper	9.74 – 80.2	1.52 – 7.20	
Zinc	6.44 – 110.4	1.40 – 9.72	
Cadmium	0.14 – 1.20	0.03 – 0.19	
Lead	1.24 – 5.05	0.28 – 1.34	
Nickel	2.71 – 11.35	0.60 - 2.84	
Cobalt	1.80 – 7.81	0.41 – 2.08	
Manganese	23.5 – 194	4.73 – 25.9	
Arsenic	0.95 – 2.71	0.27 – 1.04	
Iron	594 – 5230	88.4 – 712	

The data from this study reveal that a passive system consisting of properly selected different units can be efficiently applied under real field conditions to treat acid drainage waters.

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