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Treatment of Acid Drainage by Means of a Permeable Reactive Multibarrier

Stoyan Groudev, Plamen Georgiev, Marina Nicolova, Irena Spasova

Department of Engineering Geoecology, University of Mining and Geology, Sofia 1700, Bulgaria

ABSTRACT: Acid drainage waters with a pH of about 2.8 and containing several heavy metals (Cu, Zn, Cd, Pb, Ni, Co, Fe, Mn), radionuclides (U, Ra), arsenic and sulphates as pollutants were treated under laboratory conditions by means of a permeable reactive multibarrier consisting of two barriers connected in a series. The first barrier was a plastic column filled with crushed limestone and a mixture of solid biodegradable organic substrates (cow manure, plant compost, sewage sludge, hay). The barrier was inhabited by a diverse anaerobic microflora consisting of sulphate-reducing bacteria and other metabolically interdependent microorganisms. The water flow rate was steadily increased reflecting residence times from the initial 120 hours to 48 hours after 30 days of treatment. The concentrations of all pollutants, apart manganese, were decreased below the relevant permissible levels for waters intended for use in the agriculture and/or industry. The microbial dissimilatory sulphate reduction and the biosorption were the main mechanisms involved in the water clean-up. The manganese in the effluents from the first barrier was then efficiently removed in the second barrier by oxidation by heterotrophic bacteria producing peroxide compounds and the enzyme catalase.

ТРЕТИРАНЕ НА КИСЕЛИ ДРЕНАЖИ ПОСРЕДСТВОМ ПРОПУСКЛИВА, РЕАКТИВНА МУЛТИБАРИЕРА
РЕЗЮМЕ: Кисели дренажни води с pH около 2,8 и съдържащи различни тежки метали (Cu, Zn, Cd, Pb, Ni, Co, Fe, Mn), радионуклиди (U, Ra), арсен и сулфати, бяха третирани в лабораторни условия, посредством пропусклива реактивна мултибариера, състояща се от две последователно свързани бариери. Първата бариера представляваше пластмасова колона, пълна с натрошен варовик и смес от твърди, биологично разградими, органични субстрати (оборска тор, растителен компост, активна утайка, слама). Бариерата се характеризираше с разнообразна, анаеробна микрофлора, състояща се от сулфат-редуциращи бактерии и други метаболитно свързани микроорганизми. Дебитът постепенно се увеличаваше отразявайки контактни времена от първоначалните 120 часа до 48 часа след 30 дневно третиране. Концентрациите на замърсителите, с изключение на мангана, намаляха под пределно допустимите концентрации за води, предназначени за използване в селското стопанство и/или за индустриални нужди. Основните механизми, играещи роля в очистването на водите, бяха микробната сулфат редукция и биосорбцията. Манганът, съдържащ се във водите изтичащи от първата бариера, бе ефикасно отстранен във втората бариера, посредством окисление от хетеротрофни бактерии продуциращи прекисни съединения и ензима каталаза.

Introduction

Acid drainage water are a persistent environmental problem at many active and abandoned mine sites. These waters are generated as a result of the oxidation of pyrite and other sulphide minerals present in the relevant mineral raw materials. The oxidation is mainly a biological process carried out by the indigenous acidophilic chemolithotrophic bacteria inhibiting the sulphide mineral deposits. This process is connected with the production of sulphuric acid and the solubilization of different toxic elements such as radionuclides, heavy metals and arsenic.

Several methods for treatment of acid drainage are known but until recently only the chemical neutralization of the waters followed by the hydrolysis and precipitation of metals have been largely applied under commercial-scale conditions. Such active treatment is a high-cost operation. Its only alternative are some passive treatment systems (Cambridge, 1995; Gusek, 1995, Groudev et al., 2003). Those systems have been developed on the basis of naturally occurring biological and geochemical processes and are characterized by minimal operation and maintenance costs. The main advantage of these systems over chemical neutralization is that large volumes of sludge are not generated, the contaminants being precipitated mainly as sulphides.

Different permeable reactive barriers are among the most promising passive systems with respect to water cleanup (U.S. Environmental Protection Agency, 1998; Groudev et al., 2003). These barriers usually consist of inorganic (natural aquifer, sand, soil, gravel, limestone) and/or organic (sewage sludge, manure, plant compost, hay) components and can use both biological (mainly microbial dissimilatory sulphate reduction and biosorption) and chemical (sorption by inorganic sorbent, reaction with Fe^0) mechanisms. The construction of such barriers requires a detailed information about the geologic and hydrogeologic conditions of the relevant sites.

Some data about the treatment of acid drainage waters by means of a laboratory-scale permeable reactive multibarrier are shown in this paper.

Materials and Methods

The acid drainage waters used in this study were taken from the uranium deposit Curilo. They had a pH of about 2.8 and contained several heavy metals, radionuclides, arsenic and sulphates as pollutants. The waters were stored in refrigerator at 4°C and before use as influent into the barrier their temperature was increased to the desired level (8, 16 or 24°C). The multibarrier consisted of two barriers, which were cylindrical plastic columns with a volume of 1600 ml each. The polluted waters were directed to the barriers by means of a peristaltic pump at rates reflecting residence times varying from 120 to 24 hours.

The first barrier was anaerobic and was filled with a mixture of crushed limestone and solid biodegradable organic substrates (cow manure, plant compost, sewage sludge, hay). The barrier was inhibited by an abundant and diverse community of sulphate-reducing bacteria and other metabolically interdependent microorganisms (Table 1). The second barrier was aerobic and was filled with pieces of gravel supporting biofilms of algae and different heterotrophic microorganisms, including such able to oxidize the bivalent manganese to the tetravalent state.

The quality of the waters being treated was monitored at last once per day at the inlet and outlet of each individual barriers. Elemental analysis of the liquid samples was done by atomic absorption spectrometry and induced coupled plasma spectrometry. 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 1 l ionization chamber. Elemental analysis of the sediment samples collected from the barriers was performed by digestion and measurement of the ion concentration in solution by the above-mentioned methods. 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).

Table 1
Microflora of the water before and after their treatment by the permeable reactive barriers

Microorganisms	Acid drainage before treatment	Effluents from the first barrier	Effluents from the second barrier
		Cells/ml	
Fe^{2+}-oxidising chemolithotrophic bacteria (at pH 2)	10^6 - 10^7	0 - 10^1	ND
$S_2O_3^{2-}$- oxidising chemolithotro-phic bacteria (at pH 7)	0 - 10^1	0 - 10^2	10^2 - 10^4
Aerobic heterotrophic bacteria (at pH 7)	0 - 10^1	10^1 - 10^3	10^5 - 10^7
Anaerobic heterotrophic bacteria (at pH 7)	ND	10^5 - 10^7	10^2 - 10^4
Sulphate-reducing bacteria	ND	10^5 - 10^7	10^2 - 10^3
Methanogenic bacteria	ND	10^2 - 10^4	ND
Cellulose-degrading anaerobic bacteria	ND	10^2 - 10^6	0 - 10^2

Note: ND=not detected

The isolation identification and enumeration of microorganisms were carried out by methods described elsewhere (Karavaiko et al., 1988; Groudeva et al., 1993).

Results and Discussion

A very efficient cleanup of the waters was carried out in the first barrier (Table 2). The microbial dissimilatory sulphate reduction and the sorption of pollutants on the solid organic matter present in the barrier were the main processes involved in this cleanup. The pH of the waters was increased and stabilized in the slightly alkaline range as a result of the alkalinity produced during the sulphate reduction in the form of hydrocarbonate ions. The different heavy metals and arsenic were precipitated mainly in the form of the relevant insoluble sulphides. The hexavalent uranium was reduced to the tetravalent state and was precipitated mainly as the mineral uraninite (UO_2). Most of the radium as well as portions of the other heavy metals, uranium and arsenic were removed by sorption on the solid organic matter and were detected in the form of the exchangeable mobility fractions of the relevant pollutants. In the course of time, the initially adsorbed forms of these pollutants were turned into the less mobile and more refractory to solubilization fractions. Thus, the non-ferrous metals, iron and arsenic were detected in the oxidizable mobility fractions as the relevant sulphides. Uranium was also found mainly in this fraction in the form of uraninite. However, a part of radium was precipitated as sulphate, which was soluble in the presence of hydrocarbonate and carbonate ions and to a lower extent-in the presence of sulphuric or some organic acids.

Table 2
Data about the drainage waters before and after their treatment by the permeable reactive barrier

Parameters	Before treatment	After the first barrier	After the second barrier	Permissible levels for waters used in the agriculture and industry
pH	2.71-2.90	7.85-8.02	7.80-7.99	6-9
Dissolved O_2, mg/l	2.1 - 2.8	0.4-0.6	3.2-4.1	2
Total dissolved solids, mg/l	1144-1580	712-815	684-777	1500
Dissolved organic carbon, mg/l	0.7 - 1.0	32-73	14-21	20
SO_4^{2-}, mg/l	657-910	321-420	312-411	400
U, mg/l	2.60-3.74	<0.1	<0.1	0.6
Ra, Bq/l	0.35-0.45	<0.05	<0.05	0.15
Cu, mg/l	1.72-3.41	<0.2	<0.2	0.5
Zn, mg/l	12.5-19.8	<1.0	<1.0	10
Cd, mg/l	0.08-0.10	<0.01	<0.01	0.02
Pb, mg/l	0.41-0.77	<0.1	<0.1	0.2
Ni, mg/l	1.09-1.85	<0.1	<0.1	0.5
Co, mg/l	0.91-1.70	<0.1	<0.1	0.5
Fe, mg/l	217-352	<1.0	<1.0	5
Mn, mg/l	27.1-37.4	0.7-5.3	0.4-0.8	0.8

In the effluents from the first barrier the concentrations of all pollutants with the exception of manganese, were decreased below the relevant permissible levels for waters intended for use in the agriculture and/or industry.

It must be noted that during the first 10-15 days of treatment the concentration of dissolved manganese was also decreased below the relevant permissible level for such waters, i.e. below 0.8 mg/l, mainly by sorption of manganese on the solid organic matter. However, later this concentration increased to some extent and a tendency to fluctuations was observed. This was probably connected with a competition between the different bivalent cations for the active sites on the surface of the dead plant biomass. Only small amount of manganese precipitated in this barrier, mainly as $MnCO_3$. The effluent from the barrier were enriched in dissolved organic compounds.

These effluents were treated efficiently in the aerobic organic-bearing barrier. In this barrier the bivalent manganese was oxidized to the tetravalent state by heterotrophic bacteria producing hydrogen peroxide and the enzyme catalase. The Mn^{4+} ions were then precipitated as MnO_2. The concentration of dissolved organic compounds was also decreased as a result of their oxidation by different heterotrophs inhabiting this barrier.

The efficiency of the water cleanup depended markedly on the temperature but good results were achieved even at 4^0C, however, at longer residence times. The growth and activity of the microorganisms at this temperature were severely inhibited but the relative role played by the biosorption in the water cleanup was more essential than that during the wormer months.

The results from this study revealed that the combination of a barrier for microbial dissimilatory sulphate reduction and biosorption with a barrier for microbial oxidation of manganese and organic compounds is a suitable way to treat acid drainage waters polluted with radionuclides, heavy metals and arsenic.

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