

TREATMENT OF WATERS FROM A COPPER MINE BY MEANS OF A PERMEABLE REACTIVE BARRIER

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ABSTRACT

Acid mine waters contaminated with heavy metals (Cu, Cd, Fe), arsenic and sulphates were treated by means of a permeable reactive barrier. The barrier was constructed in a site with a high rock permeability. It represented a ditch located perpendicularly to the direction of the water flow and filled with a mixture of biodegradable solid organic substrates (leaf and spent mushroom compost, cow manure and sawdust). The barrier was inhabited by a mixed microbial community consisting of sulphate-reducing bacteria and different metabolically interdependent microorganisms. An efficient removal of the pollutants was achieved within the 18 - month experimental period during which portions of the partially exhausted solid organic substrates were periodically replaced by fresh batches of such substrates. The microbial dissimilatory sulphate reduction and the sorption of pollutants by the organic matter in the barrier were the main processes involved in this removal.

Key words: microbial sulphate reduction; sulphate-reducing bacteria; heavy metals; arsenic.

INTRODUCTION

Acid drainage waters are a persistent environmental problem at many active and abandoned mine sites. This phenomenon is connected with the oxidation of pyrite and other sulphide minerals as a result of which acidic waters containing sulphuric acid, dissolved heavy metals and solid iron precipitates are released to the environment. Toxic and radioactive elements such as arsenic and uranium are also solubilized from minerals containing these elements.

Several methods for treatment of acid mine waters exist, depending upon the volume of the effluents, the type and concentration of contaminants present. The most largely used method is connected with the chemical neutralization of the waters followed by the precipitation of metals. Such active treatment requires the installation of a plant with agitated reactors, precipitators, clarifiers and thickeners with high costs for reagents, operation, maintenance and disposal of the resulting metals laden sludge. The only alternative of such high-cost schemes are the passive treatment systems (Cambridge, 1995; Gusek, 1995; Groudev et al., 2000). These systems have been developed on the basis of naturally occurring biological and geochemical processes in order to improve the quality of the influent waters with 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.

A wide range of passive treatment systems is available currently. This paper contains some data about the treatment

of acid drainage waters from a copper mine by means of an alkalinity-producing and sulphate-reducing permeable reactive barrier.

EXPERIMENTAL

The copper ore deposit Elshiza, Central Bulgaria, for a long period of time was a site of intensive mining activities. As a result of this, a significant portion of the mine waters is contaminated with heavy metals (copper, cadmium, iron), arsenic and sulphates. The pH of these waters is acidic (usually in the range of 2.8 – 4.5) which facilitates the transportation of the dissolved contaminants.

The contaminated waters from the main underground mine in the deposit were discharged into a ravine and mixed with surface waters. The bottom of this ravine consisted of a layer of clay and different sediments and was located on weathered rocks with a high permeability down to a depth of about 3.5 m. The filtration coefficient of these rocks was in the range of about 3×10^{-3} – 8×10^{-3} m/s and there were numerous leaks in the rock matrix. As a result of this, a considerable portion of the waters infiltrated and saturated the weathered rocks. These weathered rocks were underlined by an intrusive rock with a low permeability. The filtration coefficient of this intrusive rock was about 6×10^{-8} m/s. In this way, a flow of contaminated groundwaters was formed below the bottom of the ravine. These waters were only partially separated from the surface waters in the ravine.

The permeable reactive barrier was constructed in the ravine, within the rock mass located below the bottom of the surface waters, in a site with a high rock permeability. It represented a ditch located perpendicularly to the direction of the water flow. The ditch was 5 m long, 2.5 m wide and 3.2 m deep and its bottom was located on the impermeable intrusive rock. The side walls of the ditch were covered by a corrosion-resistant cement layer to prevent the seepage of non-treated waters into the ditch. The ditch was filled with a mixture consisting of leaf and spent mushroom compost, cow manure and sawdust and was inhabited by a mixed microbial community containing sulphate-reducing bacteria and other metabolically interdependent microorganisms. (Table 1).

The ditch was covered by plastic sheets on which a 30 cm clay layer was formed. This cover efficiently isolated the surface waters in the ravine from the waters entering into the ditch through the highly permeable weathered rock.

Several piezometers were installed around and within the barrier for sampling and monitoring the process of water treatment.

Table 1 Microflora composition of the permeable barrier.

Microorganisms	Cells/ml
Sulphate-reducing bacteria	$10^5 - 10^8$
Cellulose – degrading microorganisms	$10^4 - 10^7$
Bacteria fermenting sugars with gas production	$10^5 - 10^7$
Denitrifying bacteria	$10^2 - 10^5$
Methane-producing bacteria	$10^1 - 10^3$
Anaerobic heterotrophic bacteria related to other physiological groups	$10^2 - 10^5$

Data about the waters treated in this study are shown in Table 2. The flow rate varied in the range of approximately 3 – 10 m³/24 h. It must be noted, however, that the larger mass of the barrier influents and effluents passed through the cracks and leaks in the weathered rock and not through the basic rock matrix. The quality of the barrier influents and effluents was monitored at least once per week in the period May 1997 – October 1998. The parameters measured in situ included 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.

Sulphate, nitrate and ammonium concentrations were measured photometrically. Organic substrate utilization was estimated by measuring the chemical oxygen demand (COD) of representative solid samples from the reactive barrier at the beginning and conclusion of the experiment. Cellulose was analyzed using the sulphuric acid digestion method (Updegraff, 1969). The method involves extraction with an acetic/nitric acid reagent to remove lignin, hemicellulose, and xylosans, followed by digestion with 67% sulphuric acid and final determination using the anthrone reagent.

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

Parameters	Before treatment	After treatment	Permissible levels for waters used in agriculture and industry
pH	2.8 – 4.5	7.1 – 7.5	6 - 9
Dissolved O ₂ , mg/l	0.2 – 0.6	0.1 – 0.2	2
Solids, mg/l	23 – 77	14 – 37	100
Oxidativity (by KMnO ₄), mg/l	5.1 – 12	75 – 710	40
SO ₄ ²⁻ , mg/l	824 – 1540	244 – 424	400
Cu, mg/l	3.81 – 14	<0.05	0.5
Cd, mg/l	0.15 – 1.2	<0.01	0.02
Fe, mg/l	145 – 325	<1.0	5
As, mg/l	0.37 – 2.8	<0.05	0.2

In October 1997 and in May 1998 portions of the partially exhausted solid organic substrates were replaced by fresh batches of such substrates.

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

RESULTS AND CONCLUSIONS

It was found that an efficient removal of pollutants from the waters being treated was achieved in the barrier (Table 2). Even at dilution rate as high as about 0.5 h⁻¹, the concentrations of pollutants were decreased below the relevant permissible levels for waters intended for use in agriculture and industry. This was due to different biological, chemical and physico-chemical processes but the main role was played by the microbial dissimilatory sulphate reduction. This conclusion was made on the basis of the data about the generation of hydrogen sulphide, the significant decrease of the concentration of sulphate ions and of the levels of redox potentials (Eh) as well as about the increase of the number of sulphate-reducing bacteria, the level of the pH and the content of insoluble sulphides of copper, cadmium, iron and arsenic in the barrier. The above-mentioned heavy metals and arsenic were precipitated mainly as very fine particles of the relevant sulphides. However, portions of these contaminants were precipitated as hydroxides and carbonates or were removed as a result of their sorption by the organic matter in the barrier.

The microbial community in the barrier was able to survive and to act efficiently even at the lowest pH value of the waters treated during this study, i.e. at pH 2.8. The alkalinity produced by the solubilization of the carbonates contained in the spent mushroom compost (it was characterized by a positive net neutralization potential of about 250 kg CaCO₃/t) as well as by the hydrocarbonate ions formed during the sulphate reduction gradually increased the pH and stabilized it around the neutral point.

The microbial sulphate reduction was a function of the digestibility of the organic substrates in the barrier. Different saprophytic microorganisms degraded the biopolymeric organic compounds and provided the sulphate-reducing bacteria with suitable monomeric organic sources of carbon and energy. The organic substrates used in this study were slowly degradable and supported microbial growth over the long experimental period. The concentration of dissolved organic compounds was high during the first 3-4 months after the start of the experiment (values of the permanganate oxidativity in the range of about 600 – 700 mg/l were measured during this period). Then the permanganate oxidativity was decreased, initially to about 350 – 500 mg/l and later to about 80 – 150 mg/l due to the partial exhaustion of the available easily biodegradable solid organic substrates and to the low temperatures during the cold winter months (December 1997 – February 1998). In the spring of 1998 the permanganate oxidativity started to increase and was in the range of about 200 – 250 mg/l until the end of the experiment (in October 1998). It was found that the substrate utilization was about 35% during the entire incubation period.

The temperature was an essential factor affecting the rate of both substrate biodegradation and microbial sulphate reduction. The temperature inside the barrier varied in the range of about 5 – 32°C during the different climatic seasons. The temperature coefficient Q_{10} within this range varied from 1.5 to 2.1. The maximum sulphate reduction rate achieved during this study was 190 mg/l.h. The main factor limiting the rate of the sulphate reduction was the relatively low concentrations of the electron donor (i.e. of the dissolved organic carbon). Regardless of this, the effluents from the barrier were enriched in dissolved organic compounds. The concentration of ammonium ions in the effluents was also increased considerably due to the ammonification of the organic matter. The concentration of phosphate ions was also increased and this was connected with the solubilization of a portion of the phosphate present in the spent mushroom compost. The effluents still contained high concentrations of hydrogen sulphide.

Sampling of the groundwaters after their treatment in the reactive barrier revealed that a watercourse of about 12-15 m through the rock mass was sufficient to decrease the

concentration of dissolved organic compounds, ammonia, phosphates and hydrogen sulphide below the relevant permissible levels.

It must be noted that the permeability of the rock serving as a back wall of the barrier steadily decreased due to different precipitation products (mainly fine particles of different mineral sulphides) present in the barrier effluents.

The data from this study revealed that the permeable sulphate-reducing and alkalinity-producing permeable barriers can be efficiently applied in commercial scale to treat acid drainage waters.

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