

APPLICATION OF ORGANIC MATTER FOR BIOREMEDIATION OF A COPPER ORE DUMP

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ABSTRACT

An experimental dump consisting of a low-grade rich-in-pyrite copper ore was treated to prevent the generation of acid drainage and to facilitate the processes of dump remediation. Preliminary experiments in laboratory revealed that a very efficient treatment was combining the addition of crushed limestone and organic wastes to inhibit acid generation at the upper ore layers with a clay cover to isolate the ore from the environment. Following the conclusions from these experiments, crushed limestone and mixture of waste organic substrates (spent mushroom compost, sewage sludge and plant residues) were added to the ore mass in the dump, which was previously cultivated to a depth of approximately 0.5 m. Then the surface of the dump was covered by a 15-20 cm clay layer to inhibit the penetration of rain water and air into the dump material. Finally, a 0.5 m soil layer was deposited onto the clay and was planted with leguminous plants. The above-mentioned additives caused deep changes in some essential environmental factors in the dump and in the composition of its indigenous microflora. The number and activity of the sulphide-oxidising chemolithotrophic bacteria were decreased to a great extent. After the end of the treatment (September 1996 - October 1998), the amount of rainwater penetrating into the dump and percolating through the ore mass was negligible. Furthermore, no toxic heavy metals, sulphates or other pollutants in concentrations higher than the permissible levels were found in these low-flow rate dump effluents.

Keywords: bacterial pyrite oxidation; chemolithotrophic bacteria; *Thiobacillus ferrooxidans*; acid drainage, dump capping.

INTRODUCTION

The generation of acid drainage in dumps containing mineral raw materials with a high content of sulphides (mainly pyrite) is a persistent environmental

problem. The generation of such drainage is connected with the oxidation of sulphides, which was catalysed mainly by different chemolithotrophic bacteria inhabiting these ecosystems.

Different methods to prevent acid generation from sulphidic wastes are known. Most of them are connected with the application of alkaline additives (mainly limestone) to the wastes or of engineered dry covers (Daniel and Koerner, 1993; Day, 1994; Rose and Daub, 1994; Payant et al., 1995). The alkaline additives increase the pH of the system and inhibit the activity of the acidophilic chemolithotrophic bacteria. The main advantages of the dry cover are the separation of the spoil from the environment and the prevention of water from infiltrating into the spoil mass and reacting with its constituents. However, the application of a typical impervious cover is a costly operation. For that reason, light earth covers are largely used.

In this study an experimental dump consisting of a low-grade rich-in-pyrite copper ore was treated to prevent the generation of acid drainage and to facilitate the processes of dump remediation. After careful study, a cost-effective remediation method was developed, combining the addition of crushed limestone and organic wastes to inhibit acid generation at the upper 0.5 m of the dump, with a clay and soil cover to isolate the dump from the environment. Some data from this study are presented in this paper.

MATERIALS AND METHODS

The ore dump used in this study contained about 8000 tons of a low-grade rich-in-pyrite copper ore. The dump had the shape of a truncated pyramid and was about 20 m long, 15 m wide and 10 m high. The material in the dump was run-of-mine material and ore sizes in the range of 0-50 cm were distributed through the dump.

The ore contained 2.3 % sulphur, 3.0 % iron and 0.14 % copper. Pyrite and chalcopyrite were the

main sulphide minerals in the ore. Quartz and feldspars were the main minerals of the host rock.

Preliminary experiments for studying the generation of acid drainage from the ore and the possibilities to inhibit this generation were carried out under laboratory conditions using lysimeters with an internal diameter of 30 cm and 20 cm high. Each lysimeter contained 35 kg of ore crushed to minus 15 mm. The ore used in these experiments was freshly excavated from the dump and contained its own indigenous microflora. Limestone and different solid organic substrates (spent mushroom compost, sewage sludge and plant residues) crushed to minus 2 mm were added separately or in different combinations to the different lysimeters. The lysimeters were irrigated with distilled water using different flow rates and interrupted application. The lysimeter effluents were subjected to detailed chemical and microbiological analyses. Ore samples from the lysimeters taken during and after the treatment were also analyzed.

Following the conclusions from the laboratory experiments, crushed limestone and a mixture of organic substrates (spent mushroom compost, sewage sludge and plant residues) were added to the ore mass in the dump, which was previously cultivated to a depth of approximately 0.5 m. The surface of the dump was then covered by a 15-20 cm clay layer to inhibit the penetration of rain water and air into the ore. Finally, a 0.5 cm soil layer was deposited onto the clay and was planted with leguminous plants.

Regular chemical and microbiological analyses of liquid and solid samples were carried out before and after the capping of the dump.

The procedures for isolation and identification of different microorganisms have been described elsewhere (Groudev, 1990).

RESULTS AND DISCUSSION

The lysimeter tests in laboratory revealed that the addition of crushed limestone and/or different organic substrates to the ore changed the character of the existing ecosystem, including the composition of its microbial community (Table 1). The addition of limestone only increased the pH of the ore and stabilized it around the neutral point. This sharply decreased the number of the acidophilic chemolithotrophic bacteria and practically ceased the sulphide oxidation. The mixing of the limestone with the ore caused a better effect than the addition of the limestone as a separate layer on the ore surface. It must

be noted, however, that even in the cases when the limestone was added in amounts higher than the maximum theoretically possible acid generation potential of the ore, microzones with a gradually decreasing pH were found after a certain period of time. In these microzones microbial communities consisting of chemolithotrophic bacteria able to oxidize S_0 and different sulphur compounds at alkaline, neutral and slightly acidic pH were established. Most of these chemolithotrophs were related to different species of the genus *Thiobacillus*, namely *T. thiooparus*, *T. neapolitanus* and *T. denitrificans*. It must be noted, however, that even in microzones with a pH in the range of 7 - 8 some cells of acidophilic chemolithotrophic bacteria retained their viability, although were not active under such conditions. When the pH was decreased to level lower than 4 - 4.5 these bacteria restored the oxidation of sulphide minerals.

The above-mentioned data revealed clearly that the increase of the pH to the neutral point can efficiently stop the generation of acid drainage waters but the achievement of a long-term inhibitory effect may be a costly operation.

The addition of solid organic substrates (spent mushroom compost, sewage sludge and plant residues) decreased considerably the number of the acidophilic chemolithotrophic bacteria but only after a relatively long period of time (several months). This was due to the fact that the solid substrates were refractory to biodegradation and stable microbial communities consisting mainly of different heterotrophic microorganisms developed slowly. The effect was much faster when the ore was irrigated with water containing dissolved organic compounds. However, the addition of both organic matter and limestone was the most efficient. In such system the heterotrophs were the prevalent microorganisms.

Different aerobic species, mainly such degrading the cellulose, were well represented in the upper ore layers. In the lower ore layers different anaerobic microorganisms were abundant. Some of them played an essential role in the ceasing of the bacterial sulphide oxidation. Ammonifying bacteria produced ammonia from the organic matter and in this way facilitated the maintenance of the pH near the neutral point. Sulphate-reducing bacteria also produced alkalinity (in the form of hydrocarbonate ions) and immediately precipitated any / heavy metal ions by the produced hydrogen sulphide. Furthermore, both the microbial and plant biomass displayed as efficient sorbents of such ions. It was found that the limestone consumption in the presence of organic matter was considerably lower than that in the tests in which only limestone was added to the ore.

The water content in the ore mass was the main factor determining the rate and extent of sulphide oxidation. The annual rainfall in the area, where the experimental dump was located, was about 600 mm. It was found that an irrigation rate applied on the basis of this figure was not sufficient to maintain during the whole year the humidity of the ore mass, especially in the top layers, within the levels needed for a normal microbial growth and activity. Most of the microorganisms, however, retained their viability even during the prolonged dry periods and, after rainfall, restored the oxidation of sulphides.

It was found that the addition of 20 kg crushed limestone and 20 kg crushed organic substrates per ton of ore in the top 0.5 m layer in the dump followed by the capping of the dump by means of a clay layer caused deep changes in some essential environmental factors. Within several months, the moisture of the ore was decreased to less than 15%. The oxygen content in the pore atmosphere was decreased to less than 5%, and the content of dissolved oxygen in the pore solutions was decreased to less than 0.5 mg/l. These changes resulted in deep changes in the microflora composition of the capped dump. The number of the chemolithotrophic bacteria was decreased to a great extent. The anaerobic *Thiobacillus denitrificans* only was found in a relatively higher concentration. Different anaerobic heterotrophic bacteria were the prevalent microorganisms in this ecosystem. After the end of the treatment (in September 1996) until now (October 1998), the amount of rainwater penetrating into the dump and percolating through the ore mass was negligible. Furthermore, no toxic heavy metals, sulphates or other pollutants in concentrations higher than the permissible levels were

found in these low-flow rates dump effluents.

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Table 1. Data about the effect caused by some additives on the bacterial oxidation of sulphide minerals

Index	Ore + limestone	Ore + organic substrates	Ore + limestone + organic substrates	Ore + limestone + organic substrates + clay	Control (ore only)
pH of the ore	7.1 - 7.7	3.5 - 6.0	6.8 - 7.8	6.8 - 7.7	1.7 - 2.5
Content of sulphide sulphur, %	2.1	2.0	2.2	2.3	1.4
Data about the pore solution:					
- Content of O ₂ , mg/l	6.8 - 7.8	3.2 - 6.2	6.8 - 7.9	6.6 - 7.8	1.5 - 2.5
- pH	230 - 350	82 - 210	<100	<0	350 - 570
- Eh, mV	230 - 350	82 - 210	<100	<0	350 - 570
- Total dissolved solids, g/l	3 - 12	5 - 20	2 - 6	<2	20 - 50
- Dissolved organic carbon, mg/l	2 - 7	23 - 51	44 - 120	14 - 35	3 - 7
Microorganisms (cells/g dry ore):					
- Aerobic heterotrophic bacteria	10 ²	10 ⁶	10 ⁷	10 ⁴	10 ³
- Anaerobic heterotrophic bacteria	10 ²	10 ⁵	10 ⁶	10 ⁶	10 ²
- Sulphate-reducing bacteria	10 ²	10 ³	10 ⁵	10 ⁵	10 ¹
- Fe ²⁺ -oxidising chemolithotrophs (at pH 2)	10 ²	10 ³	10 ²	10 ¹	10 ⁸
- S ₂ O ₃ ²⁻ -oxidising chemolithotrophs (at pH 7)	10 ⁵	10 ⁴	10 ⁴	10 ²	10 ²

Note: The analyses were carried out after the end of a 6 month treatment period.

Table 2. Data about the composition of the dump effluents before and after the treatment

Index	Before treatment	After treatment
pH	1.7 – 3.0	7.0 – 7.7
Total dissolved solids, g/l	15 – 44	< 2
Copper, g/l	0.28 – 1.25	< 0.005
Fe total, g/l	3.5 – 7.9	< 0.2
Sulphates, g/l	6 – 21	< 1
Dissolved organic carbon, mg/l	1.4 – 3.7	12 – 32
Microorganisms, cells/ml:		
Aerobic heterotrophic bacteria	$10^1 - 10^3$	$10^2 - 10^4$
Anaerobic heterotrophic bacteria	$10^1 - 10^2$	$10^3 - 10^5$
Sulphate reducing bacteria	$10^1 - 10^2$	$10^3 - 10^5$
Fe ²⁺ - oxidising chemolithotrophs (at pH 2)	$10^6 - 10^8$	$10^1 - 10^2$
S ₂ O ₃ ²⁻ - oxidising chemolithotrophs (at pH 7)	$10^1 - 10^3$	$10^2 - 10^3$