Mine Water and the Environment (2005) 24: 38–42 © IMWA Springer-Verlag 2005

Technical Communication

Treatment of Mine Water by a Microbial Mat: Bench-scale Experiments

A.S. Sheoran and Sushil Bhandari

Dept of Mining Eng, JNV Univ, Jodhpur, India-342011; corresponding author's e-mail: sheoranas@hotmail.com

Abstract. We investigated the treatment of acid mine drainage (AMD) by a blue-green algae-microbial consortium and substrate (containing powdered goat manure, wood chips, and soil) in 1 m^3 bench scale biological treatment test cells. The microbial mat resulted from the interaction of bacteria and filamentous blue-green algae (predominantly Oscillatoria spp). The experiments were carried out for different water column heights, and were evaluated for 24, 48, 72, 96, and 168 hours of retention. Within 24 hours of retention, the pH increased from 2.93 to 6.78 as net alkalinity went from -125 mg/L to 197 mg/L as $CaCO_3$. Turbidity decreased by 33-54%, sulphate decreased by 23-29%, and hardness decreased by 19 to 26%. We also observed that: 95% of the Fe, 79 – 97% of the Cu, 84 – 86% of the Zn, 88% of the Pb, 59 – 83% of the Co, 22 – 62% of the Ni, and 28 – 45% of the Mn were removed. A blue-green algae/microbial mat consortium may be a cost–effective treatment technique for removing metals from AMD.

Key Words: Acid mine drainage (AMD); blue green algae; metal removal; microbial mat; Oscillatoria; pollutants

Introduction

Both operating and abandoned polymetallic sulphide mines are often sources of acid mine drainage (AMD). Tailings produced by mineral processing units, equivalent to about 90% of the ore, are generally dumped in tailings impoundments; seepage from these impoundments can be a source of AMD for decades. Such AMD is often characterised by high flows and high concentrations of sulphate, heavy metals, and other toxic elements as well as low pH (Modis et al. 1998). If uncontrolled, it can contaminate surface and ground waters as well as the surrounding land. In order to alleviate the pollution, AMD can be neutralized using expensive chemicals (lime, calcium carbonate, hydrated lime, caustic soda, and soda ash), which results in the production of voluminous sludge (typically about ≈ 5% solids); disposal of this sludge is a further environmental problem and an additional cost (Chang et al. 2000; Clarke 1996; Fiset et al. 2003; Hedin et al. 1994). Thus, conventional wastewater treatment processes are often expensive, both in term of capital and operating costs. There are numerous cases where biological systems (typically passive) have been used to remove metals and other contaminants such as sulphate and heavy metals from effluent solutions by a variety of processes (Chang et al. 2000; Groudev et al. 2001; Matagi et al.1998; McCarthy et al. 1999; Michaelis 1988; Michaud 1993).

Microbial mats have been used experimentally in the U.S. to treat mine water containing metals and other pollutants (Bender et al. 1989; Bender et al. 1991; Bender 1992; Bender 1993; Bender et al. 1993). Bender and Phillips (1993) have developed microbial mats with specific microbial components for a variety of bioremediation. Mats have been reported to reduce Pb, Cd, Cu, Zn, Co, Cr, Fe, and Mn. Phillips et al. (1994) applied mats in a field remediation pilot project to remove residual manganese and iron from AMD. Mats have been found to reduce selenate to elemental selenium (Bender et al. 1991) Degradation of recalcitrant organic contaminants has also been observed under both dark and light conditions. Additional research indicatess that U^{238} can be removed from ground water samples (Bender and Phillips 1993). Microbial mats are natural heterotrophic and autotrophic communities dominated by blue-green algae. Mats are nitrogen fixing and photosynthetic (Phillips et al. 1994), and so are self-sufficient solar-driven ecosystems with few growth requirements. This study was designed to examine the feasibility of using microbial mats to remove pollutants and metals from AMD in a bench-scale experiment under controlled conditions.

Material and Methods

A 6.1 m x 3.7 m x 1.7 m basin was constructed and three coats of acid-resistant paint were applied to the inside of the basin. To generate AMD in the laboratory, 1 tonne each of powdered chalcopyrite, galena, and sphalerite, and 20 kg of pyrite was put into the basin and kept moist for 6 months. When the pH of the mixture started to decrease, additional water was added until the basin was completely filled. The whole process took 1.5 years to reach a pH close to 3. Three cement mortar bench-scale biological test cells (1 m x 1 m x 1 m) were constructed and again protected with three coats of acid-resistant paint. Sandstone pebbles (ranging up to 70 mm) were placed at the base of the test cells up to a height of 0.15 m.

The next 0.50 m of the test cells received a substrate (75% sandy soil, 20% powdered goat manure, and 5% woodchips). A thin 10 mm layer of powdered goat manure was also spread on top of the substrate. Thereafter, the rest of each test cell was filled with tap water. After 1 month, algal blooms obtained from a natural wetland receiving AMD at Khetri Copper Complex were placed in all three-test cells, along with the generated AMD, which had a pH of 3.23. Additional AMD was periodically added to all three-test cells for nearly three months until an algal bloom covered the whole area of the test cells; thereafter, it was decided to conduct the experiments.

In the first set of experiments, the height of the water column was kept at 100 mm; the height was increased to 150 mm in the second set of experiments, and to 200 mm in the third set. One L of input and 1 L of output (treated AMD) were collected in polythene jars after 24, 48, 72, 96, and 168 hours of retention.

The following parameters were examined in the laboratory: pH, electrical conductivity, turbidity, total hardness, net alkalinity (alkalinity minus acidity), sulphate, and dissolved metals. For the metals, 500 ml of filtered water samples were preserved using nitric acid and then analyzed. The pH of water samples was determined using a RI pH meter (model 151R) Buffer solutions of 4 and 7 and 9 were prepared using standard chemicals (Qualins). Electrical conductivity was measured using a meter (M.S. Electronics, model 601E). Turbidity was measured using a RI turbidimeter (model 211R). Total hardness, acidity, and alkalinity of the water samples were determined by titration. Sulphate ions were measured using the barium sulphate ($BaSO_4$) turbidimetric method. Samples were diluted prior to addition of barium chloride based on the estimated sulphate concentration so as to yield acceptable absorbance values. Blanks and standards (Na_2SO_4) were carried through the procedure to generate a standard curve, as stipulated in the method. Metal concentrations were determined using a G.B.C. atomic absorption spectrophotometer (AVANTA model). All parameters were determined as detailed in Standard Methods for the Examination of Water and Waste Water (APHA 1992).

Results and Discussion

Changes in water quality in the different experiments are given in Tables 1, 2, and 3 for various retention times. Monitoring of the treated water from the three sets of experiments revealed efficient removal of the heavy metals and other pollutants in the biological test cells after a retention time of 24 hours (Tables 4 and 5). This was due to different biological, chemical, and physico-chemical processes, but we believe that the main reaction was microbial sulphate reduction. The anaerobic sulphate-reducing bacteria produced hydrogen sulphide using dissolved organic substances as electron donors and sulphate ions as electron acceptors (Groudev et al. 2001). The net alkalinity produced during microbial sulphate reduction as well as the net alkalinity produced by the solubilisation of some acid-consuming minerals gradually increased the pH and stabilized it around neutral.

Within 24 hours of retention, turbidity was reduced up to 33.35% when the height of the water column was 100 mm, up to 42.85% when the height of the column was 150 mm, and up to 54.17% at 200 mm. The treated AMD initially reduced conductivity (up to 33.86% in the 100 mm water column experiment) but gradually values for the conductivity increased at the outlet, leading to increased conductivity in all three experiments. This increase in conductivity may be due to the release of nutrients back into the water as a result of plant decay (Mashauri et al. 2000).

Table 1. Water quality before and after different retention times in test cells with a water column height of 100 mm; samples could not be taken after 72 hours as water had been absorbed.

	Input	After 24 hours	After 48 hours	After 72 hours
pH	3.31	7.49	7.79	7.88
Conductivity, µs/cm	1515.00	1002.67	1033.00	1068.00
Turbidity, JTU	20.00	13.33	12.00	5.33
Sulphate mg/L	395	305.00	260.00	258.33
Net alk., mg/L as $CaCO_3$	-125	196.64	204.11	215.56
Hardness, mg/L as $CaCO_3$	591.85	440.55	412.37	384.18
Iron, mg/L	17.642	0.856	0.122	0.056
Copper, mg/L	14.110	0.470	0.333	0.145
Zinc, mg/L	29.100	4.113	2.367	1.673
Lead, mg/L	1.700	0.209	0.150	0.025
Cobalt, mg/L	0.300	0.050	0.033	0.017
Nickel, mg/L	0.379	0.143	0.130	0.117
Manganese, mg/L	2.010	1.453	0.733	0.340

Table 2. Water quality before and after different retention period in test cells with water column height 150 mm

Parameters	Input	After 24 hours	After 48 hours	After 72 hours	After 96 hours	After 168 hours
pH	3.23	7.68	7.80	7.83	7.93	8.21
Conductivity, µs/cm	1565.00	1108.33	1162.00	1240.67	1235.33	1317.67
Turbidity, JTU	21	12.00	6.33	3.67	3.00	1.67
Sulphate, mg/L	415	303.33	268.33	260.00	253.33	221.67
Net alk., mg/L as $CaCO_3$	-156.25	58.00	91.74	131.00	147.55	230.78
Hardness, mg/L as $CaCO_3$	623	504.47	468.73	458.35	450.93	437.77
Iron, mg/L	17.950	0.900	0.242	0.102	0.077	0.041
Copper, mg/L	14.850	0.820	0.523	0.367	0.323	0.125
Zinc, mg/L	29.500	4.524	2.820	2.382	1.150	0.376
Lead, mg/L	1.720	0.206	0.115	0.073	0.049	0.013
Cobalt, mg/L	0.330	0.110	0.083	0.063	0.053	0.043
Nickel, mg/L	0.382	0.267	0.173	0.137	0.073	0.063
Manganese, mg/L	2.200	1.213	0.957	0.827	0.707	0.360

Table 3. Water quality before and after different retention period in test cells with water column height 200 mm

Parameters	Input	After 24 hours	After 48 hours	After 72 hours	After 96 hours	After 168 hours
pH	2.93	6.78	7.34	7.36	7.43	8.66
Conductivity, µs/cm	1589.00	1044.00	1079.33	1122.67	1165.00	1479.33
Turbidity, JTU	24	11.60	4.00	3.33	2.33	2.33
Sulphate, mg/L	445	315.00	298.33	293.33	265.00	235.00
Net alk., mg/L as $CaCO_3$	-177.08	-8.08	43.80	73.44	99.30	134.78
Hardness, mg/L as $CaCO_3$	640	520.65	489.53	483.57	470.78	459.83
Iron, mg/L	17.990	0.910	0.449	0.217	0.113	0.049
Copper, mg/L	14.900	3.120	1.677	1.110	0.803	0.583
Zinc, mg/L	29.500	4.857	2.902	2.466	1.257	0.648
Lead, mg/L	1.840	0.215	0.125	0.084	0.043	0.027
Cobalt, mg/L	0.340	0.140	0.123	0.113	0.087	0.073
Nickel, mg/L	0.402	0.313	0.181	0.141	0.110	0.073
Manganese, mg/L	2.220	1.310	1.197	1.087	0.977	0.663

Table 4. Water quality before and after 24 hours of retention in test cells with 3 different water column heights

	100 mm		150 mm		200 mm	
Parameters	Before	After	Before	After	Before	After
pH	3.31	7.49	3.23	7.68	2.93	6.78
Conductivity, µs/cm	1515.0	1002.6	1565.0	1108.3	1589.0	1044.0
Turbidity, JTU	20.00	13.33	21	12.00	24	11.60
Sulphate, mg/L	395	305.00	415	303.33	445	315.00
Net alkalinity, mg/L as $CaCO_3$	-125	196.64	-156.25	58.00	-177.08	-8.08
Hardness, mg/L as $CaCO_3$	591.85	440.55	623	504.47	640	520.65
Iron, mg/L	17.642	0.856	17.950	0.900	17.990	0.910
Copper, mg/L	14.110	0.470	14.850	0.820	14.900	3.120
Zinc, mg/L	29.100	4.113	29.500	4.524	29.500	4.857
Lead, mg/L	1.700	0.209	1.720	0.206	1.840	0.215
Cobalt, mg/L	0.300	0.050	0.330	0.110	0.340	0.140
Nickel, mg/L	0.379	0.143	0.382	0.267	0.402	0.313
Manganese, mg/L	2.010	1.453	2.200	1.213	2.220	1.310

The pH values of the influent ranged from 2.93 to 3.31. The pH increased to 6.78 - 7.68 during 24 hours of retention. During daylight, the microbial mat removes CO_2 from water for use in photosynthesis and releases oxygen; this increases the pH (Groudev et al. 2001; Mashauri et al. 2000). The influent sulphate values ranged from 395 to 445 mg/L. The sulphate concentrations were decreased by 305.00, 303.33, and 315.00 mg/L, respectively, in the different water column heights of 100 mm, 150 mm, and 200 mm. The removal of sulphate gradually decreased the acidity, making the drainage alkaline. The removal rate was 22.75% to 29.21%. Net alkalinity increased from -125 to 196.64 mg/L as $CaCO_3$ during the retention period of 24 hours with a water column height of 100 mm; when the height of

Table 5. Percentage removal after 24 hours of retention in test cells with three different water column heights

	100 mm	150 mm	200 mm
Electrical conductivity	33.86	29.18	32.30
Turbidity	33.35	42.85	54.17
Sulphate	22.75	26.91	29.21
Hardness	25.57	19.03	18.65
Iron	95.15	94.99	94.94
Copper	96.67	94.48	79.06
Zinc	85.87	84.66	83.54
Lead	87.70	88.02	88.32
Cobalt	83.33	66.67	58.82
Nickel	62.17	30.10	22.14
Manganese	27.71	44.86	40.99

Table 6. Part A (effluent) of general standards for discharge of environmental pollutants, Schedule-VI (MOEF, GSR 422(E), 19.05.93), which apply to effluents such as mining and mineral processing discharges and sewage

Parameters	Inland surface water	Public sewers	Land for irrigation	Marine coastal areas
pH value	5.5 to 9.0	5.5 – 9.0	5.5 – 9.0	5.5 – 9.0
Pb, mg/L, Max.	0.1	0.1	-	2.0
Cd, mg/L, Max.	2.0	1.0	-	2.0
Cu, mg/L, Max.	3.0	3.0	-	3.0
Zn, mg/L, Max.	5.0	15	-	15
Ni, mg/L, Max.	3.0	3.0	-	3.0
SO_4, mg/L, Max.	1000	1000	1000	-
Mn, mg/L, Max	2	2	2	2
Fe, mg/L, Max	3	3	-	3

The water column was 150 mm and 200 mm, the net alkalinity increased from -156.25 to 58.00 and -77.08 to -8.08 mg/L, as $CaCO_3$. The microbial mat was highly efficient in taking up heavy metals from the AMD. Copper was always the first element to be removed, followed closely by Fe, Pb, Zn, and the other heavy metals present. Copper sulphide is highly insoluble over a broad pH range and sulphide precipitation of copper ions is therefore a rapid and efficient process in AMD. The influent load of Fe was 17.64 - 17.99 mg/L in the different water columns. Iron concentration was reduced to 0.86 mg/L, 0.90 mg/L, and 0.91 mg/L in 24 hours of retention time in the different water column heights. The removal efficiency ranged from 94.94% to 95.15% (Table 1). Influent Cu and Zn concentrations were 14.11-14.90 mg/L and 29.10-29.50 mg/L, respectively.After 24 hours of treatment, the Cu was reduced to 0.470 mg/L, 0.820 mg/L, and 3.120 mg/L, and the Zn levels dropped to 4.113 mg/L, 4.524 mg/L, and 4.857 mg/L respectively. The removal efficiency ranged up to 96.67% for Cu and up to 85.87% for Zn. Influent Pb and Co concentrations was 1.70-1.84 mg/L and 0.30-0.34 mg/L, respectively. During the retention period of 24 hours, the Pb dropped to 0.209 mg/L, 0.206 mg/L and 0.215 mg/L whereas the Co concentration dropped to 0.050 mg/L, 0.110 mg/L, and 0.140 mg/L in the different column heights; the removal efficiency ranged up to 88.32% for Pb and up to 83.33% for Co. Influent Ni and Mn concentrations ranged from 0.378 to 0.402 mg/L and from 2.01 to 2.22 mg/L, respectively. In 24 hours of retention in the cells containing the microbial mat, the Ni concentration dropped to 0.143 mg/L, 0.267 mg/L, and 0.313 mg/L whereas the Mn concentration dropped to 1.453 mg/L, 1.213 mg/L, and 1.310 mg/L at the different water column heights. The removal efficiency was 62.17% for Ni and 44.86% for Mn. Phillips et al. (1994) reported that several mechanisms, including flocculation, cell sorption, auto catalysis, and mediation of pH and oxygen concentrations, contribute to metal removal.

Conclusions

It appears that a biological treatment system with a blue-green algae/microbial mat consortium and an appropriate ratio of substrate can be used to upgrade the quality of AMD to an acceptable level. Combining algal blooms and a bacterial system in simulated constructed wetland systems effectively raised the pH and produced virtually metal-free effluents with very low acidity. Pollutants were removed efficiently and the residual concentration in the wetland test cells were decreased below the relevant permissible level (Bureau of Indian Standards (Table 6) and Ministry of Environment and Forests) after 24 hours of retention, except for lead, where the input concentration was high. It was observed that most of the improvement took place within 24 hours of retention time; it continued up to 168 hours, but the rate of improvement slowed. Water column height played a role but was not very significant.

The substrate, which contained powdered goat manure and wood chips, was effective for culturing algae in AMD in our bench-scale experiments and appeared to accelerate sulphate reduction. With this mixed substrate, pH increased and heavy metals were removed. It may be feasible to stimulate bacterial sulphate reduction in water-filled mines and open pits. Sulphide precipitation of heavy metals has some important advantages over hydroxide precipitation, including lower solubility of metal sulphides over a broad pH range.

This was a preliminary study; a detailed study is needed to properly design algal mat-assisted constructed wetlands and to choose aquatic plants to optimally treat industrial and other domestic wastewater in India. For a developing country like India, passive treatment systems, which have no energy requirements, are preferred. Microbial mat treatment is relatively simple to operate and maintain; local people can easily be trained to do it. Thus, this method would appear to be a cost effective treatment plan for AMD, and an alternative to active treatment. Phillips et al. (1994) conducted similar experiments in AMD from coalmines and obtained similar results.

References

American Public Health Association (APHA) (1992) Standard methods for the examination of water and waste water, 18th edit, APHA New York

Bender J, Archibold ER, Ibeanusi V, and Gould JP (1989) Lead removal from contaminated water by a mixed microbial ecosystem. J Wat Sci & Tech 21(12): 1661-1664.

Bender J, Gould JP, Vatcharapijarn Y and Saha G (1991) Uptake, transformation and fixation of Se(VI) by a mixed selenium-tolerant ecosystem. J Wat Air and Soil Pollution 59:359-367

Bender J (1992) Recovery of heavy metals with a mixed microbial ecosystem. Final report, U.S. Bureau of Mines, Grant G0190028

Bender J (1993) Biological effects of cultured cyanobacteria mats on water contaminants. Report #1 U.S. Env. Protection Agency, Grant CR8168901

Bender J, Murray R, Phillips P (1993) Microbial mat degradation of chlordane. In: Means JL, Hinchee RE (Eds) Emerging Technology for Bioremediation of Metals, Lewis Publ, Boca Raton, FL, p 135-139

Bender J, Phillips P (1993) Implementation of microbial mats for bioremediation. In: Means JL, Hinchee RE (Eds) Emerging Technology for Bioremediation of Metals, Lewis Publ, Boca Raton, FL, p 85-98

Chang IS, Shin PK, Kim BH (2000) Biological treatment of acid mine drainage under sulphate – reducing conditions with solid waste materials as substrate. J Wat Res 34 (4): 1269-1277

Clarke L (1996) Coal mining and water quality. J Mines Metals and Fuels, p 181-183

Fiset JF, Zinck JM, Nkinamubanzi PC (2003) Chemical stabilization of metal hydroxide sludge. Proc, 10th International Conf on Tailings and Mine Waste, AA Balkema Publ, Oct 12-15, Vail, CO, USA, p 329-332

Groudev SN, Georgiev PS, Angelov AT, Spasova II, Mitrov T (2001) Treatment of metal-contaminated waters by a pilot-scale constructed wetland. International Symp on Univ Ropet 2001, Petrosani, Romania, Oct 18-20, http.//www.labmet.ntua.gr/enviman/publications.html

Hedin RS, Nairn RW, Kleinmann RLP (1994) Passive Treatment of Coal Mine Drainage. USBM IC-9389, U.S. Bureau of Mines, Pittsburgh, PA, 35 pp

Mashauri DA, Mulugu DMM, Abdul Hussein BS (2000) Constructed wetland at the University of Dar Es Salaam. J Wat Res 24 (4): 1135-1144

Matagi SV, Swai D, Mugabe R (1998) A review of heavy metal removal mechanisms in wetlands. Afr J Trop Hydrobiol Fish 8: 23-35

McCarthy D, Bullock R, Pantano J (1999) Evaluation of wetland treatment for the removal of metals from mining impacted groundwater. Proc, 9th International Conf on Tailings and Mine Waste, AA Balkema Publ, Rotterdam, Netherlands, p 725-733

Michaelis HV (1988) Integrated biological systems for effluent treatment from mine and mill tailings. In: Salomons W, Forstner U (Eds), Management of Solid Waste, Springer-Verlag Publ, NY, p 99-113

Michaud LH (1993) Passive treatment and control methods for acid mine drainage. In: Bawden A (Eds) Innovative Mine Design for the 21st Century, p 747-756

Modis K, Adam K, Panagopoulas K, Kontopulos A (1998) Development and validation of a geostatistical model for prediction of acid mine drainage in underground sulphide mines. Trans Instn Min Metall, sect A, pp 102-107

Phillips P, Bender J, Simms R, Rodriguez S, Britt C (1994) Manganese and iron removal from coal mine drainage by use of a green algal – microbial mat consortium. Proc, 3rd International Conf on the Abatement of Acidic Drainage, USBM SP 06A-94, Pittsburgh, PA, April 24-29, p 99-109

Submitted Dec 1, 2004; accepted Dec 29, 2004