



hydrometallurgy

Hydrometallurgy 71 (2003) 217-225

www.elsevier.com/locate/hydromet

# Acid reduction using microbiology: treating AMD effluent emerging from an abandoned mine portal

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#### Abstract

The performance of a microbial treatment system, partially implemented, receiving abandoned mine portal effluent in the gold mining district of Nova Lima, Minas Gerais, Brazil is documented. The system consists of four oxidationprecipitation-settling ponds and three microbial treatments ponds operating in series. The mine portal effluent flow volume averaged 0.6 L s<sup>-1</sup>, increasing during the rainy season to 1.0 L s<sup>-1</sup>. The portal effluent pH ranged from 1.4 to 3.4, measured between 1995 and 2001. The particle-settling rates specific to the portal effluent were 25-3.9 g m<sup>-2</sup> day<sup>-1</sup>, which decreased from the oxidation-precipitation ponds A-D. Most of the pyrite oxidation and subsequent iron hydrolysis to iron hydroxide occurred in the underground workings. The resulting weathering products were flushed out during high flows. For these effluents, the function of the oxidation ponds was mainly iron hydroxide particle removal. Oxidationsettling ponds were necessary to prevent or reduce iron coating of the limestone and organic carbon. From oxidationsettling pond D, the effluent flowed into a series of microbial treatment ponds. These ponds were "seeded" with 10 t of raw potatoes and 4.5 t of whole sugar cane. These ponds were designed to have a floating cattail cover to reduce turbulence and stabilize anaerobic sediments, which will form, and provide a continuous organic carbon source to the sediments. However, at the time of writing, the cattail cover was not yet functional. The pH of discharge from the microbial treatment ponds ranged from 4.5 to 7.2 between June 1999 and June 2001. The as-yet incomplete treatment system however, removed on average 37-87% of the monthly Ni load (0.6-1.7 kg month<sup>-1</sup>), 77-98% of Al load (19-49 kg month<sup>-1</sup>), 74-82% of Zn load (1.7-0.6 kg month<sup>-1</sup>), and 78-95% of Fe load (71-236 kg month<sup>-1</sup>). © 2003 Elsevier B.V. All rights reserved.

Keywords: Acid mining drainage; Passive treatment; Inactive mine working; Biological polishing; Acid reduction using microbiology

### 1. Introduction

Acid mine drainage (AMD) originating in abandoned mine workings can persist for a very long time. Chemical treatment plants generate large volumes of

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secondary wastes (metal-laden sludge), which require disposal. Alternative, more natural means for treatment of AMD effluent can be developed, which generate low volumes of environmentally stable iron hydroxide sludge or yellow-boy. Such treatment systems utilize chemical—physical reactions (oxidation/precipitation) and biologically mediated reactions to increase pH. Those processes facilitate metal coprecipitation (mainly with Al and Fe) and/or adsorption on

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organic or inorganic particulate matter, which settle to the sediment in the treatment ponds. In the deeper portions of the sediment, where low Eh values prevail along with high pH values, bio-mineralization renders the metals stable (Ehrlich, 1990; Fyson et al., 1998; Kalin and Smith, 1997; Kalin et al., 1995, 1999). Boojum Research has developed one such alternative treatment system based on these general concepts and supported, in part, by the MEND program of the Canadian government (Kalin, 1993).

The design for a passive treatment system was developed to treat the seepage from the Copper Cliff tailings in Sudbury, Canada in 1989. By 1992, the key design criteria for such a passive system had been determined (Kalin, 1993). The result of 4-year performance covering the years after completion between 1993 and 1996 was reported (Kalin et al., 1999). The design consisted of initial oxidation-precipitationsettling ponds to oxidize and then precipitate the iron hydroxide. Once most of the iron is removed, the effluent passes through a series of microbial treatment cells. These consist of cells with two organic sediment surfaces, the first, on the bottom of the cell, and the second, on top of the cell, provided by a floating cattail cover. The upper organic cover provides organic carbon for microbial metabolism, lowers cell

turbulence, and allows the reducing region of the lower sediment to move up into the water column. The greater the volume of water upon which the microbial system can operate, the more efficient the cell. A completed treatment cell, with both upper and lower covers, has been called an Acid Reduction Using Microbiology (ARUM) cell or pond.

The experience gained at the Copper Cliff tailings seepage system was utilized to design the full-scale Brazilian treatment system. The main difference between the two systems, which affects the performances, is the difference in the degree of iron oxidation in the seepage to be treated. The Copper Cliff tailings seepage emerges at the foot of the tailings dam in a highly concentrated, reduced form with a neutral pH value. The effluent from Brazilian underground workings is more dilute and has a low pH value when it emerges from the portal. Other differences between a completed treatment system and the below-described Brazilian system include the following: (1) As of this writing, the organic cattail cover was not yet in place, and (2) raw potatoes and raw sugarcane were added to the treatment cells to 'kick-start' the microbial treatment, providing reducing conditions due to organic decay. Because of these two differences, we did not have a fully functional system.

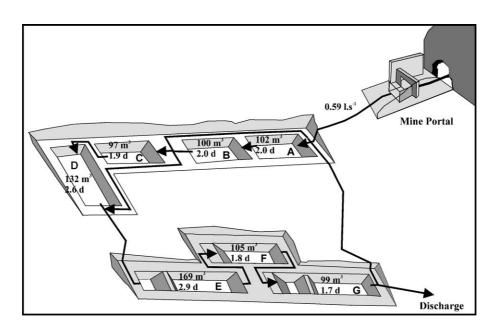


Fig. 1. Layout of treatment system, including estimated volume (m<sup>3</sup>) and residence time (days) for each pond.

# 2. Treatment system layout construction description

The layout of the system is given in Fig. 1. Ponds A–D were used as oxidation–precipitation–settling ponds, followed by ponds E–G where ARUM treatment was partially installed. The floating vegetation cover was not yet completely in place. The volumes of the ponds ranged from 97 to 169 m³ with theoretical residence times ranging between 1.7 and 2.9 days. Most ponds had a similar area (approximately  $17.5 \times 8.5 \times 1.0 - 1.5$  m deep, with the exception of ponds D and E, which were larger) (Fig. 1). The mountainous terrain in part dictated the pond size. The pipe leading from pond G back into pond D was constructed in case insufficient treatment took place and the effluent had to be recirculated prior to discharge.

Each pond is lined with very durable plastic (Hyperlon-like) secured with sandbags at the edges and interconnected with pipes. Originally, the microbial treatment ponds' gravel berms, which were designed to distribute the entering flow, were composed of coarse (3–5 cm diameter) gneiss gravel. These berms plugged during heavy rains, as the banks surrounding the pond system had not been stabilized with vegetation. Those berms were replaced by limestone gravel (5 cm diameter) to assist treatment during the start-up phase. A total of 10 t of raw potatoes and 4.5 t of whole sugar cane were added to the three ARUM ponds to provide organic carbon and form microbial active sediments. The living floating cattail cover will prevent oxygenation of the water column, enhance reducing conditions, and supply new organic carbon to the newly forming sediments. Once the oxidation-precipitation rates specific to the portal effluent from the underground workings are determined, the system can be adjusted appropriately to optimize treatment capacity (Liu and Kalin, 1994).

## 3. Sampling and analytical methods

All ponds were monitored monthly at their outflow for water chemistry and flow by Morro Vehlo staff. Measurements of pH and electrical conductivity were performed in the field. Samples were stored in a refrigerator and filtered within 24 h of collection. Samples were filtered using 0.45-µm filters, acidified with nitric acid, and analyzed by ICP at the analytical laboratory of MMV/AngloGold in Nova Lima. The laboratory followed standard QA/QC procedures, regularly analyzing spiked and blank samples.

Sedimentation rates of particulate matter were determined by suspending vertically clear polycarbonate tubes about 0.5 m below the water surface. The tubes had a diameter of 5 cm and a length of about 25 cm and were held in place along a rope that spanned across the pond. Two tubes were suspended in each cell for 68 days. The collected solids in the tubes were dried and weighted to determine the rate of solids settling per square meter per day. The solids were acid digested, and the MMV/AngloGold laboratory analyzed their elemental contents.

#### 4. Results and discussion

# 4.1. Seasonal effluent characteristics

The water emerged from the portal and was contained in a pipe that feeds pond A. Pond A was considered representative of portal effluent. The distance between the portal and pond A was short (approximately 40 m). With the exception of peak flows in January (76 m³ day⁻¹), flows from the portal were relatively steady over the remainder of the year (29–58 m³ day⁻¹). The period of lowest flow occurred between May and November (53 m³ day⁻¹) and increased between December and April (68 m³ day⁻¹). The concentrations of sulfate and iron, as well as electrical conductivity measured in the water in pond A, the inflow of the system, are plotted seasonally from August 1999 to June 2001 in comparison to those in pond G, the outflow of the treatment system (Fig. 2).

In Fig. 2, the seasonal pattern of the sulfate concentrations reveals that during the rainy season, the concentrations were high with 1500 mg  $L^{-1}$  between November and February, but considerably lower over the rest of the year at 400 mg  $L^{-1}$ . Similarly, the electrical conductivity of the effluent was high during the rainy season with values 2600  $\mu S$  cm $^{-1}$  from November through February and lower during the dry season, decreasing to approximately 1000  $\mu S$  cm $^{-1}$ . Sulfate values very closely follow the seasonal trends of iron, with higher values

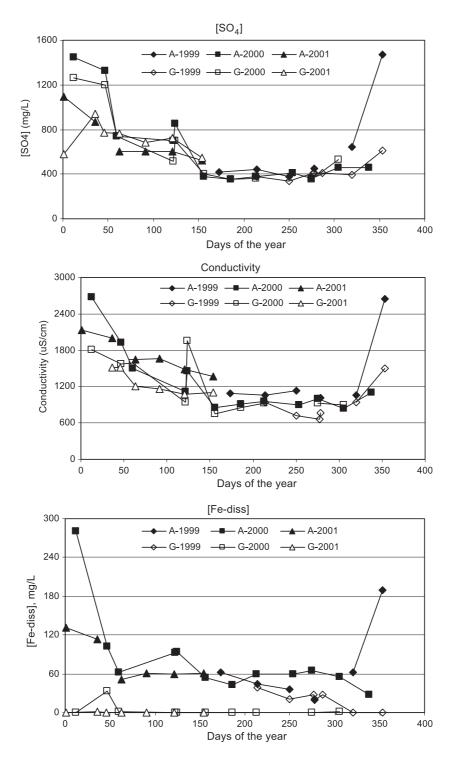


Fig. 2. Seasonal changes in [SO<sub>4</sub>], Conductivity and [Fe-dissolved] at ponds A and G.

during high flows, suggesting that previously oxidized weathering products were flushed out of the underground workings. If this was not the case, the higher flows during the rainy season should dilute the portal effluent, and the concentrations would be lower than in the dry season. As the microbial treatment ponds in the system did not yet have effective reducing conditions due to the absence of the floating vegetation cover, the sulfate concentration in pond G, the outflow, was nearly the same as in pond A, the inflow. Electrical conductivity showed the seasonal pattern well, but did not change much between inflow and outflow of the system.

The seasonal patterns of sulfate and iron concentrations as well as the electrical conductivity (Fig. 2) suggest a reasonably steady rate of weathering of the pyritic material in the underground workings. High flows carried accumulated weathering products from rock walls and from the underground workings where water was stagnant during the dry season. Oxidation of pyrite and hydrolysis of iron hydroxide took place in underground workings as the effluent emerges at a low pH value. The oxidation ponds of the treatment system were therefore used primarily to settle iron hydroxide particles.

# 4.2. The oxidation-precipitation ponds performance

The first step of natural water cleansing took place in ponds A-D, leaving the effluent with lower metal content and slightly lower pH. Coprecipitation and/or adsorption of metals probably also occurred during this first step. This step is especially important when arsenic is present in the effluent, which is often associated with gold ores. In this treatment stage, the opportunity exists to "trap" arsenic during the process of iron hydroxide formation (Wagemann, 1978). Arsenic was detected in the analyses of the solid material collected in the sedimentation traps, but not in the water. Concentrations in the water were probably too low to detect at current detection limits (<0.01 or <0.04 mg  $L^{-1}$ ).

The data from the oxidization-precipitation ponds are summarized in Table 1. The pH of the portal effluent entering pond A averaged 2.5 and did not vary much more than 1 pH unit through the next three ponds. From ponds A to D, a slight increase in conductivity was evident, but the acidity decreased from an average

Table 1 Sedimentation and elemental removal rates in oxidation-precipitation ponds

		Pond A	Pond B	Pond C	Pond D
рН (1995-	N	28	23	23	23
2001)	min	1.4	2.3	2.3	2.4
	max	3.4	3.1	3.1	3.1
	avg	2.53	2.75	2.73	2.75
Conductivity	N	27	23	23	23
(µS/cm)	min	541	1030	1039	1032
(1995 -	max	2670	2650	2620	2610
2001)	avg	1357	1514	1526	1469
Acidity	N	24	23	23	23
(mg/L,	min	185	177	177	156
CaCO <sub>3</sub> )	max	1597	1298	1298	1298
(1995 -	avg	430	412	402	399
2001)					
Sedimentation	rate (a m -	$\frac{2}{2} dav^{-1}$			
Scaimentation	rate (g m	25	8	6	4
		23	O	O	7
Elemental con	centration in	ı sedimen	0	ls	
Fe	%	45.9	47	46.8	45.9
$Al_2O_2$	%	1.67	1.27	1.46	2.05
Zn	$\mu g/g$	66	55	75	65
Ni	$\mu g/g$	35	39	44	49
Cu	$\mu g/g$	47	50	67	77
As	$\mu g/g$	175	233	222	193
Removal rates	(pond surfa	ice area 1	$7.5 \times 8.5 m$	)	
Fe Fe	kg	50.7	m.621 8.0		
	month <sup>-1</sup> pond <sup>-1</sup>	30.7	111.021 0.0		
Zn	kg	0.0073	0.0019	0.0020	0.0011
Zii	month <sup>-1</sup>	0.0073	0.0017	0.0020	0.0011
	pond <sup>-1</sup>				
Ni	kg	0.0039	0.0014	0.0011	0.00086
141	month <sup>-1</sup>	0.0057	0.0014	0.0011	0.00000
	pond <sup>-1</sup>				
Al	kg	1.16	0.28	0.24	0.23
	month <sup>-1</sup>	1.10	0.26	0.24	0.23
	pond <sup>-1</sup>				
Cu	kg	0.0052	0.0018	0.0017	0.0013
Cu	month <sup>-1</sup>	0.0032	0.0016	0.001/	0.0013
	monun pond <sup>- 1</sup>				
Ag		0.010	0.0082	0.0058	0.0024
As	kg	0.019	0.0082	0.0038	0.0034
	month <sup>-1</sup>				
	pond <sup>-1</sup>				

of 430 to 399 mg L<sup>-1</sup> CaCO<sub>3</sub> equivalents, indicating that some metals were removed.

The sedimentation traps were suspended in the ponds from August 20 to October 27, 2000. During the 68 days, 3.3 g of dry weight material was collected in pond A and 0.5 g in pond D. These

values resulted in sedimentation rates of 25 g m<sup>-2</sup> day<sup>-1</sup> to 4 g m<sup>-2</sup> day<sup>-1</sup>, decreasing from ponds A to D. In addition to settling, iron hydroxide particles formed encrustments of various consistencies on all underwater surfaces. Bacteria and algae also colonized those surfaces, forming iron-rich biofilms. Plastic curtains were placed in ponds A and B to enhance surface area and biofilm formation (Fig. 3). To what degree these curtains and the biofilms assisted in removing iron hydroxides was not quantified. Therefore, the measured sedimentation rates do not quantify the entire iron-removal process.

The elements which were found in the sedimented particles were Fe, Al, Zn, Ni, Cu, and As. The main components of the suspended material were clearly the hydroxides Fe and Al (Table 1). They accounted for nearly 50% of the settling matter. The concentrations of Zn were similar in all ponds, ranging from 55 to 75  $\mu$ g g<sup>-1</sup>. Ni concentrations seemed to increase from pond A with 35  $\mu$ g g<sup>-1</sup> to pond D with 49  $\mu$ g g<sup>-1</sup>. Similarly, Cu concentration increased from 47  $\mu$ g g<sup>-1</sup> in pond A to 77  $\mu$ g g<sup>-1</sup> in pond D. Arsenic in the solids was highest in ponds B and C, with 233 and 222  $\mu$ g g<sup>-1</sup>. The metal distributions suggest that during further hydrolysis with the concurrent pH depression, release of Ni and Cu occurs.

With the sedimentation rates and the elemental content, it was possible to estimate the metal removal from the water in each pond. Most of the iron was removed from pond A (50.7 kg month<sup>-1</sup> pond<sup>-1</sup>) through pond D (8.0 kg month<sup>-1</sup> pond<sup>-1</sup>). The highest removal was also noted for the metals in ponds A and B (Table 1). Thus, most of the metals and contaminants were removed from the system in the first two ponds.

#### 4.3. Overall system performance

In Fig. 4, the elements are plotted seasonally, where clear differences in concentrations existed between inflow and outflow of the system. The pH of the final discharge of pond G averaged 6.1. This pH improvement was impressive given that the pH entering the microbial treatment ponds from pond D was 2.7. This increase was only partially due to microbial activity, as the pipe entering the ponds leads through the coarse limestone berms.

Pond D discharges acidity to the ARUM ponds about 400 mg L<sup>-1</sup> CaCO<sub>3</sub> equivalents during the dry season, but no acidity (<1 mg L<sup>-1</sup> CaCO<sub>3</sub>) remains in pond G when the final effluent leaves the treatment system during both high and low flows (Fig. 4). The addition of organic material to the ARUM ponds provided extensive surface area, which resulted in Fe and Al being completely removed. Although the metals Zn, Ni, and Cu were generally low entering the microbial treatment ponds, some additional removal took place (Fig. 4). Metal removal might improve



Fig. 3. Curtains in pond A.

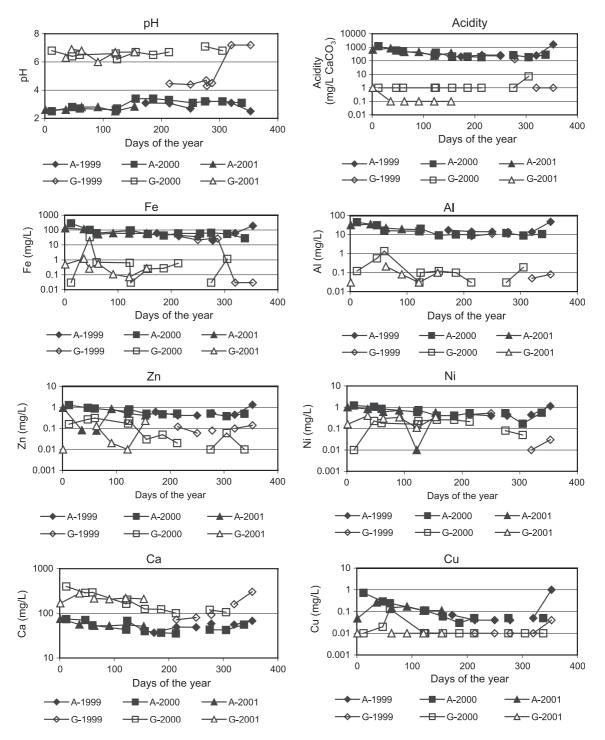


Fig. 4. Comparison of water chemistry between ponds A and G.

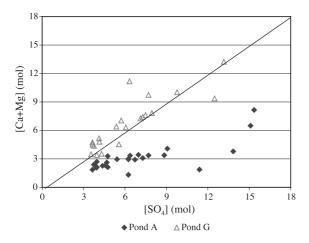


Fig. 5. Molar ratio of  $SO_4$  to Ca + Mg, 1995 - 2001 (n = 48).

further with establishment of full reducing conditions in the ARUM ponds. Due to the placement of limestone as flow diffusers around the pipes at the entrance of the ARUM ponds, Ca concentrations increased at the discharge point.

Calcium and magnesium left the treatment system from pond G as either gypsum or epsom salts. The importance is that the metals changed from a sulfate-reactive form at low pH in pond A to a nonreactive form. The expected molar ratio of 1:1 between sulfate and the sum of Ca and Mg was very close for most of the samples in the final discharge (Fig. 5). The samples with very high excess free sulfate compared to Ca and Mg in pond A occurred during the high flow season.

The volume of water and the metal concentrations passing through the ponds were used to determine the effectiveness of the metal removal at each stage of the treatment process. The metal load estimates were calculated using average concentrations of elements and flows (flow times concentration), integrating those values between measurement periods. In Table 2, metal loads are presented for Fe, Zn, Ni, Al, and Cu, differentiating between the metal load for the high- and low-flow months. During the rainy season, portal effluent discharged 236 kg of iron per month, of which 15% was removed in oxidation-precipitation ponds A-D and 95% of the remaining iron was removed in the incomplete ARUM ponds. During the non-rainy season, the system removed 78% of the iron. The Al load was also removed more effectively during the rainy season when 98% of Al was removed by the treatment system, while only 77% was removed during the dry season. The pattern of removal was quite different for the Zn, Ni, and Cu loadings which increased between ponds A and D, although the loads are low. This would be expected, as some oxidation and hydrolysis of the effluent took place, as indicted from the range of pH values measured in the oxidation-precipitation ponds (Table 1). However, the AR-UM ponds removed the metal load effectively, reaching higher removal rates for Ni, Al, and Cu in the rainy season than in the dry season. The ARUM ponds work very efficiently in terms of Zn and better in the dry season. The reasons for these differences are not clear presently.

Table 2 Seasonal changes in elements of water in treatment system

Metal	(1999–2000)	Pond A effluent (kg month <sup>-1</sup> )	Pond D (kg month <sup>-1</sup> )	Pond G (kg month <sup>-1</sup> )	Pond D removal (%)	Pond G removal (%)
Fe	December-April	236.1	202	11	15	95
	May-November	71.4	44	16	38	78
Zn	December-April	1.71	1.83	0.440	<b>-7</b>	74
	May-November	0.69	0.69	0.123	0	82
Ni	December-April	1.70	1.73	0.226	-2	87
	May-November	0.63	0.69	0.398	<b>-9</b>	37
Al	December-April	49.0	51.2	0.88	<b>-5</b>	98
	May-November	18.9	17.6	4.27	7	77
	December-April	0.71	0.86	0.08	-21	88
	May-November	0.10	0.11	0.02	<b>-6</b>	85

December – April: rainy seasons, flow = 68 m<sup>3</sup>/day. May – November: non-rainy seasons, flow = 53 m<sup>3</sup>/day. Future work includes additional curtains in the oxidation-precipitation ponds, installing the floating cattail cover, and converting one of the oxidation-settling ponds to a microbial treatment pond.

#### 5. Conclusion

The first 2 years of operation of the full-scale ARUM treatment system performed better than anticipated. This performance was largely due to the excellent engineering and construction of the facility, good flow control, the limestone gravel berms, and the systematic regular monitoring of water quality. This data set allowed us to assess the performance of the first treatment step, the oxidation-precipitation ponds. The seasonal effluent characteristics indicate the ferrous iron oxidation and hydrolysis take place mainly in the underground workings. Because most of the precipitation-settling was done in the first two ponds (A and B), pond D could probably be converted to an ARUM pond to further increase microbial treatment. Further work can be carried out to improve iron removal in the first three ponds by adding more curtains. The floating vegetation cover should be completed in order to improve metal removal and provide stable conditions for the precipitates. Overall, the performance assessment indicates that this system represents a suitable ecological engineering approach to the treatment of AMD discharged from abandoned workings in the Nova Lima mining district, where water characteristics are similar in mineralogy to the Esperanca underground workings.

# Acknowledgements

We thank the civil engineers Elcio Barbosa and Renato Pinheiro of AngloGold/AngloAmerican who were involved during the engineering and construction of the system. We also thank MMV/AngloGold for providing the funds to construct the system. The MMV analytical laboratory provided excellent support, and the commitment of Irany Braga is particularly appreciated.

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