REMEDIATION PROPERTIES OF MATERIALS TO TREAT ACID MINE DRAINAGE WATER AT A GOLD MINE OPERATION IN BRAZIL [1]

by

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Abstract. Many constructed passive treatment systems have been implemented throughout the United States for treatment of acid mine drainage either in operational mines or at abandoned mine sites. However, only in the last 10 years have the issues related to acid mine drainage become a concern for both the mining sector and environmental agencies in Brazil. This project evaluated the remediation properties of suitable substrate materials for an anaerobic treatment system in a gold-mine operation. An ideal passive treatment system utilizes local materials to compose a substrate that will be the source of carbon and energy for bacterial growth of the sulfate-reducing bacteria. In this experiment, the chemical characteristics of candidate materials for an anaerobic system substrate were studied, individually and in mixtures. Substrate materials included fresh and aged manure, alfalfa, hay, begas, sawdust, limestone, and iron filings. These materials were chosen according to a similar study developed by *Gilbert et al. (1998)* and considered for their chemical nature and properties. Substrate performance was evaluated through arsenic and sulfate removal and pH and Eh variation during a six-week period. Mixtures containing iron filings, alfalfa, manure and hay presented the best results for arsenic and sulfate removal, higher pH, and a reducing environment. When sawdust/begas were substituted for manure/hay, the pH of the system dropped and the performance decreased.

Additional keywords: sulfate reducing bacteria, bioremediation, zero valent iron.

Introduction

Research on the remediation properties of materials to treat acid mine drainage water[1] was conducted at RPM – Rio Paracatu Mineracao, Morro do Ouro Gold Mine, in Paracatu, Minas Gerais-State, Brazil, during a six week period, starting on March 11, 2000. RPM is a Rio Tinto open-pit mine that has been in operation since December 1987. In 1998, the company started mining and processing a sulfidic ore (pyrite and arsenopyrite -1% sulfur and 2500 ppm of As, on average). Environmental impact studies for the mining and processing of the sulfidic ore identified impacts related to this new operation. Consequently appropriate mitigation and control measures were designed and implemented. An extensive in-house acid rock drainage (ARD) study, *Taboada et al. (1997)*, had determined that low levels of sulphur (0.3% on average) and arsenic (800 ppm) in the tailings would result in the gradual elevation of sulfate and arsenic levels in the tailings decant water as the dam filled. As a precaution, the company planned to install an ion exchange plant if concentrations of arsenic and sulfate in the tailings dam drain water approached the pre-determined safety levels. The company decided recently to consider passive

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Table 1. Tailings Dam Water Quality

Fe Total mg/L	Fe Sol. mg/L	As Total mg/L	As Sol. mg/L	Zn Sol. Mg/L	Cu Sol. Mg/L	Cd Sol. mg/L	Mn Sol. mg/L	Sulfate Mg/L
0.85	< 0.01	0.34	0.27	0.03	0.007	< 0.001	0.30	200

Table 2. Substrate Code Key

Material	Code
Alfalfa	A
Begas	B
Iron Filings	F
Hay	H
Inocula (fresh cow manure)	I
Limestone	L
Manure (aged)	M
Sawdust	S

treatment as an innovative and more cost-effective and environmentally sound alternative for the treatment of arsenic and sulfate from the tailings dam water.

Objectives

The research objectives were to 1) identify materials near the mine that would be suitable to be used as a substrate in an anaerobic treatment system; 2) determine the chemical characteristics of substrates; and 3) identify mixtures of substrates that are more efficient in the removal of arsenic and sulfate from water.

Methods and Materials

Tailings Dam Water Quality

The tailings decant water is typically of good quality (Table 1): near neutral pH (6.4), oxidizing environment Eh (100 mV), and low iron and moderate sulfate concentrations (<0.01 mg/l and 200 mg/L, respectively). However, because the arsenic level is relatively high (0.34 mg/L), the water is inappropriate for direct discharge into the downstream creek. The results of an analysis of water from the tailings dam Sampling Point 3 (SP-3) on March 11, 2000, are given in Table 1. The chemical analyses of filtered (0.45 μm) and acidified samples were conducted by ICP-Plasma (metals), HGG-As (arsenic) and turbidimetry (sulfate) according to the SMEWW 3120B, SMEWW 4500 standards at the Lakefield-Geosol laboratory in Belo Horizonte, Brazil.

Chemical Characteristics of Substrate Materials

A constructed passive treatment system is designed to mimic natural wetlands. As such, materials used to construct the system need to have chemical and/or physical characteristics that will provide a similar natural environment for desirable bacterial activity and associated geochemical reactions. In this research the chosen substrate materials included the following:

Limestone. Limestone dissolves to provide alkalinity to the system, contributing to the achievement of a basic requirement for an anaerobic system to work properly (pH > 5.5).

Iron Filings. Iron filings strongly contribute to the formation of a reducing environment as $Fe^{(0)}$ is oxidized to Fe^{2+}, and possibly provides additional metal adsorption sites. Thus, iron filings are best considered as zero valent iron (ZVI). Oxidation of iron filings produces H_2 gas and hydroxyl ions that contribute to the increase of alkalinity. *Gu et al. (1999)* found that H_2 gas formed during iron filings corrosion stimulated the growth of microbial populations and increased sulfate reduction during column experiments.

Organic Matter. Organic matter (manure, sawdust, alfalfa and hay) provides low molecular weight organic acid compounds that provide carbon sources for new bacterial cell synthesis. Also, microorganisms derive energy and reducing power from the oxidation reactions, where electrons are removed from the substrate and transferred to the terminal electron acceptor. The organic matter provides sites for adsorption. Organic materials such

Table 3.Substrate Composition

Sample		Composition					
		Fe	LS	ORGANIC 1	ORGANIC 2	INOCULUM	H20 ML
1	L	-	15	-	-	-	100
2	H	-	-	15 g	-	-	100
3	M	-	-	15 g	-	-	100
4	S	-	-	15 g	-	-	100
5	F	15 g	-		-	-	100
6	A	-	-	15 g	-	-	100
7	B	-	-	15 g	-	-	100
8	FASI	30 g	-	20 g	40 g	10 g	300
9	FHSI	30 g	-	20 g	40 g	10 g	400
10	FBSI	30 g	-	20 g	40 g	10 g	300
11	FLASI	15 g	15 g	20 g	40 g	10 g	300
12	FLHSI	15 g	15 g	20 g	40 g	10 g	400
13	FLBSI	15 g	15 g	20 g	40 g	10 g	300
14	FASI	45 g	-	20 g	25 g	10 g	300
15	FBSI	45 g	-	20 g	40 g	10 g	300
16	LBSI	-	30 g	20 g	40 g	10 g	300
17	LASI	-	30 g	20 g	40 g	10 g	300
18	LHSI	-	30 g	20 g	40 g	10 g	400
19	FAMI	30 g	-	20 g	40 g	10 g	300
20	FBMI	30 g	-	20 g	40 g	10 g	300
21	FAMI	45 g	-	20 g	25 g	10 g	300
22	FBMI	45 g	-	20 g	25 g	10 g	300
23	FSMI	40 g	-	25 g	25 g	10 g	300
24	FHSI	45 g	-	10 g	30 g	10 g	300
25	FM	50 g	-	50 g	-	-	300
26	LM	-	50 g	50 g	-	-	300
27	FASI	30 g	-	30 g	40 g	-	300
28	FASI	30 g	-	20 g	40 g	10 g	300
29	FBSI	30 g	-	20 g	40 g	10 g	300
30	FASI	45 g	-	20 g	25 g	10 g	300
31	FBSI	45 g	-	20 g	25 g	10 g	300
32	FAM	30 g	-	20 g	50 g	-	300
33	FBM	30 g	-	20 g	50 g	-	300
34	FAM	45 g	-	20 g	35 g	-	300
35	FBM	45 g	-	20 g	35 g	-	300

as manure provide the bacterial inocula that operate in the passive treatment system.

Determination of Substrate Composition

Based on previous research, it was decided that the substrate would contain between 0% to 10% by weight fresh cow manure (inocula) and approximately 40% to 70% mixed organic matter (hay, alfalfa, sawdust, begas). The remainder would be a combination of iron filings and limestone. In total, 35 samples of pure and mixed materials were prepared and tested for six weeks. Sample codes are shown in Table 2.

Substrate Preparation

Most of the materials were collected from sources within a radius of approximately 10 km of the mine area, except hay, which was bought from a feed store in Brasilia (240 km from the mine). The materials were taken to the RPM Environmental Department ARD Research Laboratory, weighed in different fractions, mixed, and put in one-gallon Ziploc bags. Water from the tailings dam (Sampling Point - 3) was added (100mL to 400 mL, depending on the composition of the mixture). Table 3 presents the composition, by weight, of each sample. Note that ORGANIC I is the second letter in the substrate code. In the 35 samples prepared, Eh and pH were measured weekly, together with observations of odor, color and formation of precipitates/bacteria film. After a six-week period, some samples were chosen for assessment of their remediation properties according to qualitative observations and Eh/pH results. For the chosen

Table 4. Eh and pH values of the test samples

Sample		pH					Eh				
		12/03/00	28/03/00	11/4/00	18/04/00	25/04/00	12/03/00	28/03/00	11/4/00	18/04/00	25/04/00
1	R - L	7.7	7.3	6.9	6.7	6.9	10	171	197	220	203
2	R - H	5.0	5.5	5.3	6.2	6.8	20	-94	86	-178	-275
3	R - M	6.9	7.4	7.1	6.8	7.1	25	-47	72	-96	-153
4	R - S	4.8	4.8	4.9	4.7	4.6	80	160	136	68	89
5	R - F	7.0	6.8	6.9	6.2	7.8	-600	-118	-527	-688	-764
6	R - A	5.7	5.3	6.2	5.1	4.9	-155	-87	-122	-28	-19
7	R - B	2.8	3.6	5.4	5.6	5.9	175	142	15	-58	-48
8	FASI	6.1	5.7	7.1	6.7	6.7	-510	-128	-208	-208	-188
9	FHSI	5.7	5.7	6.9	6.6	6.4	-620	-126	-171	-188	-180
10	FBSI	5.4	5.5	5.3	5.3	5.4	-360	-78	16	-48	-80
11	FLASI	6.4	5.7	6.9	6.8	6.7	-425	-98	-129	-178	-174
12	FLHSI	6.0	5.7	7.2	7.1	6.7	-625	-88	-184	-197	-158
13	FLBSI	6.0	5.9	6.0	5.8	6.3	-410	-78	-22	-82	-122
14	FASI	6.3	5.8	7.3	6.8	6.8	-405	-142	-160	-161	-168
15	FBSI	5.3	5.9	5.5	6.1	6.2	-350	-78	-16	-148	-164
16	LBSI	6.1	7.1	7.1	6.8	6.3	-395	-228	-86	-116	-102
17	LASI	6.4	7.0	7.4	7.2	6.9	-415	-216	-226	-122	-132
18	LHSI	6.2	6.8	7.3	7.1	6.7	-485	-212	-198	-72	-120
19	FAMI	6.5	7.3	7.6	7.3	7.1	-515	-234	-236	-232	-236
20	FBMI	6.4	6.8	7.0	6.9	6.5	-270	-198	-184	-159	-188
21	FAMI	6.6	6.4	7.5	7.4	7.2	-665	-90	-226	-208	-232
22	FBMI	6.1	6.3	6.8	6.8	6.4	-375	-112	-186	-220	-194
23	FSMI	7.0	7.4	7.0	7.0	6.3	-430	-180	-168	-180	-318
24	FHSI	6.6	5.8	7.0	7.0	6.6	-450	-80	-161	-208	-197
25	FM	7.6	7.8	7.3	6.9	6.4	-715	-112	-312	-204	-370
26	LM	7.3	7.8	7.4	6.9	6.7	-30	-97	-88	-122	-142
27	FASI	6.4	6.2	7.0	6.9	6.8	-640	-87	-178	-182	-206
28	FASI	6.3	6.1	7.0	6.9	6.6	-475	-78	-148	-160	-178
29	FBSI	5.6	5.6	5.4	4.9	5.0	-220	67	14	32	-16
30	FASI	6.3	6.0	7.1	6.9	6.3	-610	-78	-225	-180	-144
31	FBSI	5.9	6.0	5.9	6.1	5.8	-620	-74	-78	-108	-116
32	FAM	6.5	7.5	7.7	7.6	6.9	-490	-248	-268	-314	-228
33	FBM	6.3	6.5	7.1	6.8	6.3	-273	-128	-168	-490	-198
34	FAM	6.8	7.5	7.8	7.3	7.0	-660	-248	-216	-340	-256
35	FBM	6.3	5.8	6.9	6.4	6.2	-330	-88	-160	-178	-178

samples, chemical analysis was undertaken by ICP-Plasma (metals), HGG-AS (arsenic) and turbidimetry (sulfate).

Results and Discussions

Table 4 presents the pH and Eh evolution for all samples during the six-week period. Begas, sawdust, hay and alfalfa generated the lowest initial and final pH, probably due to the availability of low molecular weight organic acids. Begas and sawdust samples particularly exhibited very low pHs at the beginning of the experiment (2.4 and 4.8, respectively). Also, begas and sawdust had high initial and final Eh's when compared to the other materials. On the other hand, limestone, iron filings and manure exhibited high pH values throughout the experiment, with iron filings showing the highest pH at the end of the test period (7.8). Iron filings also produced the lowest Eh levels at the beginning and end of the experiment (-600 mV and –764 mV, respectively), demonstrating their ability to produce a very reducing environment. Manure helped establish a reducing environment in the system, initially producing near-neutral Eh levels that decreased gradually with time.

Table 5. Concentrations of metals in the final waters for some test samples

Sample	Fe Total Mg/L	Fe Sol. mg/L	As Total Mg/L	As Sol. mg/L	Zn Sol. mg/L	Cu Sol. mg/L	Cd Sol. mg/L	Mn Sol. mg/L	Sulfate mg/L
Raw Water	0.85	< 0.01	0.34	0.27	0.03	0.007	< 0.001	0.30	200
1 - L	< 0.05	< 0.05	<0.01	<0.01	0.02	<0.01	0.002	<0.02	-
5 - F	3.45	0.83	<0.01	<0.01	0.28	0.03	<0.001	0.08	-
8 - FASI	33.6	1.43	<0.01	<0.01	0.14	< 0.01	0.004	<0.02	-
11 - FLASI	11.5	4.73	<0.01	<0.01	0.05	0.01	0.005	0.05	-
12 - FLHSI	19.7	11.8	<0.01	<0.01	0.03	< 0.01	0.003	<0.02	-
14 - FASI	9.45	0.37	<0.01	<0.01	0.03	< 0.01	<0.001	<0.02	6
17 - LASI	2.43	< 0.05	0.05	0.03	0.03	< 0.01	0.003	<0.02	-
18 - LHSI	0.15	0.15	0.07	0.06	0.06	< 0.01	0.005	0.06	4
19 - FAMI	11.1	6.19	<0.01	<0.01	0.02	< 0.01	0.002	<0.02	-
21 - FAMI	17.1	0.36	<0.01	<0.01	0.03	0.02	0.002	<0.02	2
26 - LM	0.48	<0.05	<0.01	<0.01	<0.01	< 0.01	0.001	<0.02	35
27 - FASI	13.8	8.69	<0.01	<0.01	0.02	< 0.01	0.001	<0.02	-
29 - FBSI	413	319	<0.01	<0.01	0.12	< 0.01	0.022	13.2	-
34 - FAM	15.5	11.1	<0.01	<0.01	<0.01	0.01	<0.001	<0.02	-

Substrates containing sawdust and begas (samples 10, 13, 15, 29 and 31) typically exhibited lower pH values, and although the Eh is initially low, it increases over time, reaching near zero values at the end of the experiment (Table 4). Therefore, these substrates are not expected to provide good contaminant removal. Conversely, the substrates that did not contain begas and/or sawdust (19, 21, 25, 26, 32 and 34) typically had the highest pH values throughout the experiment (pH > 6.5) and lowest Eh values as well. The substrate containing only iron filings and manure (25) produced the highest pH values and the most reducing environment at the beginning and end of the experiment (-715 mV and –370 mV, respectively). Some white-grayish/black film-mass, which could be bacteria or precipitate, was observed in the first week, even in samples that were not inoculated (25, 26, 32, 33, 34 and 35) but contained aged cow manure in the substrate composition. This may be an indication that aged cow manure could have been another source of bacteria. However, these precipitates could also be siderite and/or other precipitated ferric-ferrous hydroxides, depending on the Eh-pH in the system. Preliminary observations suggested the following:

- Substrates that contain both sawdust and begas may not be able to provide an appropriate environment for anaerobic bacterial activity (low pH, high Eh).
- Iron filings, manure and limestone, if present in the substrate, contribute to the establishment of an adequate environment for anaerobic bacterial activity.

In similar experiments, *Gilbert et al. (1999)*, where iron filings were not used, and depending on the water chemistry, pH and Eh usually evolved gradually (as pH increased, Eh decreased) over time, until the system stabilized. However, in this research, the initial Eh was very low and increased gradually, probably due to the presence of iron filings and their enhanced oxidation by the presence of carbonate and sulfate, according to *Gu et al. (1999)*. In samples containing ZVI, the initial redox potential started at a very low level (-700 mV to – 300 mV) and increased gradually over time, reaching approximately the same observed levels (0 to –200 mV) in experiments without ZVI, after a period of six weeks. It is likely that some contaminants are instantaneously removed due to the reactions occurring in the presence of the ZVI. *Lackovic et al. (2000)* reported arsenic removal in an abiotic system, containing only ZVI at near neutral pH. At a later stage, removal of contaminants may occur as a consequence of reactions caused by bacterial sulfate reduction and precipitation of arsenic sulfide together with ZVI oxidation.

Rochette *et al. (2000)* reported that arsenate reduction by hydrogen sulfide is very rapid at pH=4 but very slow at neutral pH. *Gu et al. (1999)* found that sulfide was formed as a result of microbial reduction of sulfate that became significant after about two months of column operation. This may suggest that arsenic removal in a biotic system in the presence of ZVI may occur faster than in a biotic system devoid of ZVI. Further research is necessary for a better understanding of how a passive system works under these conditions.

Table 5 shows the chemical analysis of the water from 14 samples that were selected as good candidates for contaminant removal based on the Eh/pH and qualitative observations. We were particularly interested in arsenic and sulfate removal. It can be seen that arsenic was below the detection limit used (0.01 mg/L) in all samples except those that did not contain iron filings (substrates 17 and 18). For these two samples, the removal efficiency of soluble arsenic was 89% and 78%, respectively. Therefore, it seems that an anaerobic system containing ZVI is more effective at removing arsenic than a system without ZVI.

Due to the amount of water available at the end of the tests, a sulfate analysis was possible only on samples 14, 18, 21 and 26. The best sulfate removal (99.9%) was obtained by substrate 21 FAMI (mixture of iron filings, alfalfa, manure and inocula), which did not contain begas or sawdust. This test achieved pH and Eh values varying between 6.2 to 7.5 and -665 to -232 mV, respectively. Very good sulfate removal was also obtained by substrates 14 FASI (97%) and 18 LHSI (98%), indicating that sawdust is not detrimental to sulfate removal, as long as the pH is above 5.5 and a reducing environment is established. Also, test 18 LHSI exhibited very good sulfate removal, even in the absence of ZVI.

Substrate 29 FBSI (pH 4.9 to 5.6 and Eh=-220 to +32 mV) produced the highest levels of soluble metals (Zn, Cd and Mn). It appears that they could have been dissolved from particulates in the tailings water due to the conditions (Eh / pH) in the system or come from the sawdust/begas. Generally, substrates with begas/sawdust showed a higher concentration of metals than the substrates where these materials were absent and iron filings, alfalfa, and manure were present.

Conclusions

Results obtained during the six-week study, suggested the following:

- The substrates containing begas/sawdust showed the highest levels of metals in solution, probably due to the lower pH and higher Eh values in the system.
- The substrates containing iron filings, alfalfa and manure typically presented the lowest levels of metals in water.
- Iron filings provide an immediate reducing environment that may boost the bacterial activity at the beginning of the test.
- The presence of iron filings in the substrates also resulted in complete arsenic removal (below detection limit of 0.01 mg/L) when compared with substrates that did not contain ZVI.
- The presence of sawdust and begas does not limit sulfate removal, as long as the system provides an adequate environment for sulfate reduction (pH > 5.5 and reducing environment).
- The best sulfate removal was obtained in the substrate 21-FAMI, which contained iron filings, alfalfa, manure and inocula.
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