LABORATORY EXPERIMENTS DESIGNED TO TEST THE REMEDIATION PROPERTIES OF MATERIALS[1]

By

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Abstract. Passive treatment systems constructed to remediate mine drainage have proven to be very successful for a wide variety of drainage compositions and volumes. The construction of an anaerobic passive treatment system requires a mixture of local materials with the objective of producing a system that allows adequate water flow while supporting the growth of sulfate-reducing bacteria. These bacteria have the effect of reducing the oxidizing potential in the system causing many sulfide-forming metals in solution to precipitate. The focus of these experiments was the study of chemical characteristics of materials, individually and in mixtures, with the purpose of determining which would be best suited for incorporation into a treatment system. The materials of interest were manure (fresh and aged), alfalfa, limestone, and sawdust, which were all collected in close proximity to the construction site of the proposed treatment system. A variety of chemical and physical hypotheses were formulated prior to performing simple chemical characterization and anaerobic treatment tests. The hypotheses relating to the chemical nature of the single materials were carbon to nitrogen ratio, availability of low molecular weight organic acids, number of adsorption sites, and organic carbon content. In addition, hypotheses concerning the performance of mixtures were evaluated by looking at the relative amount of bacterial growth (and metal removal) seen in each mixture over a 4-week period. The results of the laboratory experiments confirmed the hypotheses, and demonstrated that in the mixtures, the anaerobic bacteria flourish when alfalfa is present, up to a point. The best mixture that allowed proliferation of bacteria while also removing metals consisted of 50% limestone, 25% aged manure, 15% sawdust, and 10% alfalfa (% by weight).

Additional Key Words: bioremediation, constructed wetlands, mine drainage.

Objectives

The objectives of this research were to determine the contamination/remediation properties of single materials and mixtures using two types of experiments: simple chemical characterization tests and anaerobic treatment tests. The ultimate goal was to obtain a composition suitable for use in an anaerobic passive treatment system.

Site Information

The mine water in question is issuing from the Belle Eldridge adit. Field indicators seem to suggest the Belle Eldridge adit water is of reasonably good quality: low ionic conductivity (450 µs/cm), reasonable alkalinity (120 mg/L), pH of 6.6 (good for sulfate reducers), low Fe and Al (armoring not a potential problem), and presence of life in drainage channel. Inductively coupled plasma – atomic emission spectroscopy (ICP –AES) analysis of filtered and acidified samples provided the following composition (mg/L): Al, 0.06; Ca, 68.32; Cd, 0.05; Cu, 0.02; Fe, 0.44; K, 1.32; Mg, 14.88; Mn, 0.30; Na, 1.73; SO_4, 97.28; and Zn, 4.51. All experiments used this mine drainage, referred to as DR.

Chemical Hypotheses

Substrate Materials

Limestone. Assuming it contains 90 % $CaCO_3$, its dissolution will further contribute to alkalinity.

Waste Rock. The material is benign and will not contribute to the degradation of the water in a treatment system. Chemical characterization/assessment tests will confirm or deny this.

Aged Materials. Lowest carbon to nitrogen ratio (C/N) - in order of increasing C/N: dairy farm aged manure, livestock aged manure, alfalfa, sawdust. This can be somewhat verified by placing the materials in de-

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ionized water and then measuring the pH. If the solution is acidic, the most likely source is carboxylic acids suggesting a high C/N ratio.

Availability of low molecular weight organic acids beneficial to sulfate reducers – in order of increasing availability: sawdust, dairy farm aged manure, livestock aged manure, alfalfa. Younger materials would be expected to have more of these acids; therefore, acidic pH values indicate increasing availability while high ionic conductivities infer amount (Wildeman and Updegraff 1998).

Number of adsorption sites - in order of decreasing number: dairy farm aged manure, livestock aged manure, alfalfa, sawdust. This can be verified by measuring the ionic conductivity of a 2:1 water to substrate mixture. A higher ionic conductivity correlates to a larger number of adsorption sites.

Organic C content - in order of decreasing organic C: alfalfa, sawdust, manure, limestone

Physical Hypothesis

The construction of a bench scale treatment system presents a complex hydrologic situation in terms of the substrate mixture (Gusek et al. 1998, Wildeman et al. 1993). If a single material forms a continuous phase, then pore spaces, and thus, hydraulic conductivity, are controlled by this material. The materials ranked in order of decreasing hydraulic conductivity from high: washed limestone, unwashed limestone, alfalfa, sawdust, aged manure (low). If alfalfa forms a continuous phase in the presence of abundant manure, then the breakdown of alfalfa could decrease the hydraulic conductivity considerably. If manure ever becomes a continuous phase, a major problem could result because there would most likely be minimal flow through the system.

Integration of Substrate Chemical/Physical Hypotheses into Anaerobic Experiment Design

In order to determine which substrate mixtures would be best suited for a bench scale system, the chemical and physical nature of each substance has to be considered together. The objective is to produce a system that allows adequate water flow while supporting the growth of sulfate reducers by supplying food for energy and growth.

Using the hypotheses above, it was decided that no mixture would consist of less than 50% by weight limestone, and all would contain 5% inocula (anaerobic, sulfate reducing bacteria). The remaining 45% would be a mixture of alfalfa, sawdust, and manure in these "best guess" proportions – in order of decreasing confidence:

1) 25% manure, 10% sawdust, 10% alfalfa
1a) 25% manure, 15% sawdust, 5% alfalfa
2) 25% alfalfa, 20% sawdust
2a) 15% manure, 15% sawdust, 15% alfalfa
3) 30% sawdust, 15% alfalfa
3a) 30% alfalfa, 15% manure
4) 30% sawdust, 15% manure
4a) 30% manure, 15% sawdust
5) 45% sawdust
5a) 45% manure

Methodology

The laboratory samples were all named using the codes found in TABLE 1, the substrate code key. All materials were used as is except for the two aged manure and the four mine waste samples which were all put through a minus 10-mesh sieve to obtain a more representative sample. The mine drainage used (see General Hypotheses for composition) was from an unfiltered "macro" sample taken from the Belle Eldridge adit. Electrochemical field instruments were used to measure pH, Eh, and ionic conductivity. Only the pH and Eh meters required regular calibration. The pH meter was standardized before each set of analyses using pH 4 and 7 buffer solutions. Eh measurements were obtained by measuring a Light's solution before analysis, and then applying a correction based on the Light's to the measured value. These same calibration procedures were used throughout the suite of laboratory experiments.

Chemical Characterization

Two types of characterizations were done: 1) Initial experiments which entailed measuring pH, Eh and conductivity of a single material mixed with de-ionized water, and 2) Contamination/remediation assessment of inorganic (rock) samples using pH, Eh, and ICP – AES analytical data.

Initial experiments. Involved mixing 50 g of substrate with 100 mL of de-ionized water, a 2 to 1, water to substrate ratio. After ½ hour and 23 hours, pH, Eh, and ionic conductivity measurements were taken with field instruments.

Contamination assessment of inorganic samples. (numbers 1 through 15) Required 100 g of each solid material. Half (50 g) was mixed with 200 mL of de-ionized water, and the other half was mixed with 200 mL of adit drainage. Samples were placed in one-quart ziploc bags, and measurements of pH and Eh were

TABLE 1. Substrate Code Key		
Code	Name	Description
WLW	waste rock west	Composite waste rock from west side of pile.
WLE	waste rock east	Composite waste rock from east side of pile.
WC	waste rock clay	Composite waste rock rich in clay.
LW	washed limestone	Washed limestone, Lien & Sons.
LU	unwashed limestone	Unwashed limestone, Lien & Sons.
MD	dairy manure	~3 yr. old manure samples, Ward Dairy Farm.
MF	feedlot manure	~10 yr. old manure samples, St. Onge Livestock.
IM	manure inoculum	Wet manure sample-liquid waste pond, Ward Dairy Farm.
IB	bog inoculum	Muck collected from Spruce Creek area, below Lexington adit.
SD	Sawdust	Approximately 10 yr. old sawdust (pine), Langer Sawmill.
DI	de-ionized water	De-ionized water from CSM.
DR	drainage water	Belle Eldridge adit, collected after overnight storm.
TL	Tailings	Tailings from mill area.
AF	Alfalfa	Alfalfa hay provided by BLM, South Dakota.
U	un-inoculuated	No sulfate reducing bacteria inoculum added.

TABLE 2. Anaerobic Sample Mixtures - % by Weight[1]					
Sample	LW	MD	MF	SD	AF
IMDR20	100 g of substrate to characterize chemically.				
IMDR20a					
MDDR21					
MDDR21a					
MFDR22					
MFDR22a					
IBDR23					
IBDR23a					
MDAFSD24	50	25	-	10	10
MDAFSD24a	50	25	-	10	10
MDSDAF25	50	25	-	15	5
MDSDAF25a	50	25	-	15	5
SD26	50	-	-	45	-
MD27	50	45	-	-	-
AFSD28	50	-	-	20	25
SDAF29	50	-	-	30	15
SDAFMD30	50	15	-	15	15
AFMD31	50	15	-	-	30
SDMD32	50	15	-	30	-
MDSD33	50	30	-	15	-
SDMF34	50	-	15	30	-
MFSD35	50	-	30	15	-
SDMDU36	50	20	-	30	-
MDSDU37	50	35	-	15	-
SDMFU38	50	-	20	30	-
MFSDU39	50	-	35	15	-

[1]Percent of total solid weight, 100 grams.

taken weekly for one month. After this time, 10 mL aliquots were centrifuged, filtered (0.45μm), spiked with 1 ppm Sc (internal standard), and analyzed by ICP - AES.

Anaerobic Experiments (samples 20 through 39)

These experiments were carried out in a manner similar to those of Wildeman et al. 1994a, 1994b. Most samples were prepared by mixing (in one quart ziploc bags) 200 mL of adit drainage with 100 g of a substrate mixture containing 50 g of unwashed limestone, 5 g of inocula, and 45 g of alfalfa, sawdust, and manure in various combinations. The exceptions to this were samples 36 – 39 which contained no inocula, thus 5 g more manure, and samples 20(a) – 23(a) which contained 100 g of a single material and 200 mL of adit drainage. These exceptions were prepared to chemically characterize the materials, and to see if any contained sulfate reducing bacteria. Also, samples 28 and 31 were placed in 1-gallon bags containing a total of 300 mL of drainage to compensate for the water absorbed by the large amount of alfalfa. TABLE 2 displays the compositions of all the anaerobic samples prepared.

Observations of color, odor, and peculiarities, along with pH and Eh measurements were taken every week for one month. After one month, 10 mL aliquots were centrifuged, filtered (.45μm), spiked with 1 ppm Sc (internal standard), and analyzed by ICP – AES.

Important to note is that on 5/22, an analysis of the drainage water used in the above mixtures was obtained and indicated that there was a sulfate deficiency. Seeing as how this could hamper growth of the sulfate reducing bacteria, all duplicates (ending in "a") and those samples containing no manure were spiked with Na_2SO_4. Approximately .15 g of solid Na_2SO_4 (100 mg SO_4) was added to each, giving a SO_4 concentration of 500 mg/L.

TABLE 3. Initial Experiment Results – ½ hour

Sample	pH	Eh[1]	Conductivity[2]
WLE	2.96	555	416
WLW	7.20	338	221
WC	8.30	250	115
TL	3.59	444	2140
MF	9.08	203	4020
MD	8.63	233	4080
IM	8.71	230	2430
AF	6.08	375	3220
SD	4.09	473	68.2
LU	9.38	188	66.1

[1]Eh units are milli-volts (mV).
[2]Ionic conductivity in micro-Siemens per cm (μS/cm).

TABLE 4. Chemical Assessment of Inorganic Materials- Concentrations in mg/L

Sample	As	Mn	Pb	Zn
WLEDI1	0.051	0.393	0.041	3.057
WLWDI2	0.110	0.028	0.157	0.273
WCDI3	BDL[1]	0.039	BDL	0.067
LWDI4	BDL	BDL	BDL	BDL
LUDI5	BDL	BDL	BDL	BDL
TLDI6	0.027	1.154	0.770	2.249
WLEDR7	0.043	0.901	BDL	6.135
WLWDR8	0.042	0.005	BDL	0.077
WCDR9	BDL	0.007	BDL	0.061
LWDR10	BDL	BDL	BDL	0.202
TLDR12	0.022	1.283	0.290	4.464
WLEDI13	0.032	0.331	0.037	2.436
WLEDR14	0.043	0.649	0.045	6.436
DR15	BDL	0.326	BDL	1.781
DR15A	BDL	0.386	BDL	0.488

[1]BDL – Below detection limit

Results and Discussion

Chemical Characterization

The results of the initial experiments are very useful in evaluating the accuracy of the substrate materials hypotheses presented above (TABLE 3). The results after 23 hours were not significantly different than those at ½ hour; therefore, they are not reported. The substance with the largest C/N ratio, as evidenced by the low pH, proved to be sawdust followed by alfalfa and the two aged manure samples. This is the same trend seen for availability of low molecular weight organic acids. Ionic conductivities in the thousands of μS/cm produced by both manure samples and alfalfa demonstrate that these materials have the largest number of adsorption sites, especially relative to sawdust which produced very low conductivities. It is important to note the very low pH produced by waste rock east (WLE) and the tailings (TL), a result which indicates that some of the materials are fairly reactive and could contribute to the degradation of a treatment system, if incorporated. The chemical assessment using ICP – AES data corroborates this preliminary finding.

Table 4 displays the concentration of As, Mn, Pb, and Zn (mg/L) after one month's time in solution. All samples ending in "DI" contained the material of interest and de-ionized water; therefore, the numbers basically represent the change in concentration of the metal for the specific material of interest. The pH, Eh, and conductivity of the samples did not change significantly over the one-month period, and were not very different from the values in TABLE 3. The results of the initial experiments (TABLE 3) and the contamination assessment of inorganic materials (TABLE 4) allowed two important conclusions: 1) All of the waste rock and tailings around the mine site are not suitable materials for a treatment system. 2) The limestone is suitable; no major differences found between washed and unwashed samples. The main consideration in these conclusions was the ICP data (TABLE 4) which showed that some of the materials contain considerable amounts of readily available contaminants – Mn, Pb, and Zn – to name a few important ones.

Anaerobic Experiments

The weekly pH and Eh results found in TABLE 5 show that some of the mixtures are better than others in allowing proliferation of the sulfate reducing anaerobes. The negative Eh values and the large jump in Eh from week 3 to week 4 in some samples, especially 24 and 25, are signs that the bacteria are thriving, consuming oxygen, and causing a decline in oxidation potential. Figure 1 displays the change in Eh over the 4-week period for samples 24 and 25. The graph shows the rapid change in Eh that occurred in the duplicate samples (ending in "a") after additional sulfate was added on 5/25. Other signs of bacterial growth are H_2S presence and the formation of a black film (the bacteria), observations which were found in some samples. As aforementioned, samples ending in "a" were all

TABLE 5. Anaerobic Experiments - pH and Eh Results

	pH				Eh (mV)			
Sample	5/8	5/15	5/22	5/29	5/8	5/15	5/22	5/29
IMDR20	7.42	7.36	7.34	7.56	-98	-118	-61	-81
IMDR20a	7.42	7.31	7.35	7.61	-84	-118	-62	-125
MDDR21	7.46	7.13	7.3	7.49	-103	-116	-110	-92
MDDR21a	7.54	7.44	7.55	7.52	-12	-127	-121	-122
MFDR22	7.55	7.49	7.57	7.54	-89	-72	-53	-58
MFDR22a	7.46	7.36	7.54	7.60	-109	-88	-70	-109
IBDR23	6.14	5.51	5.82	6.14	27	62	62	69
IBDR23a	6.26	5.86	5.65	6.11	79	70	144	152
MDAFSD24	5.57	5.88	6.49	7.45	-26	-25	-44	-119
MDAFSD24a	5.63	6.03	7.22	7.47	-41	-27	-35	-156
MDSDAF25	5.73	6.17	7.17	7.52	-82	-50	-44	-84
MDSDAF25a	5.69	5.91	6.93	7.43	-54	-45	-67	-101
SD26	6.50	6.30	6.53	6.77	30	150	40	-22
MD27	7.60	7.34	7.47	7.49	-86	-19	-73	-95
AFSD28	5.30	5.41	5.79	6.86	48	32	5	-22
SDAF29	5.12	5.73	5.68	6.21	97	12	51	-44
SDAFMD30	5.49	5.60	6.22	6.62	16	27	-31	-11
AFMD31	5.28	5.42	5.65	6.16	90	99	84	13
SDMD32	6.94	6.92	6.89	7.18	180	10	68	71
MDSD33	7.22	7.29	7.26	7.33	-29	-10	18	35
SDMF34	6.73	6.73	6.96	6.99	29	12	38	43
MFSD35	7.22	7.20	7.14	7.42	14	-52	4	66
SDMDU36	6.59	6.89	7.05	7.09	137	78	-41	-12
MDSDU37	7.12	7.24	7.34	7.53	150	22	-36	34
SDMFU38	6.65	6.84	7.10	7.18	159	149	-39	35
MFSDU39	7.40	7.41	7.22	7.44	-26	124	78	-73

spiked with Na_2SO_4, which, being food for the bacteria, should have caused an increase in populations and thus, more negative Eh values relative to the un-spiked samples. This is exactly what was seen (TABLE 5 & Figure 1) in most of the duplicate samples. Important to note are the low Eh numbers for samples 20 through 23 (un-inoculated) which show that manure inoculum (IM), dairy manure (MD), and feedlot manure (MF) are all potential sources of anaerobic bacteria. All three "a" samples had lower Eh values than sample 25 which was inoculated. It is expected that those samples most suitable for bacterial growth (low Eh) will be most effective at reducing the concentration of metals in solution. This is because the low Eh would presumably cause precipitation of various metal sulfides.

ICP – AES results (TABLE 6) show that the mixtures which had the lowest Eh values were those that removed the most metal from solution, in this case, Zn. The samples that were spiked with Na_2SO_4 (100 mg SO_4) seemed to show more metal removal relative to the un-spiked samples, especially samples 24 and 25. The S concentration in some of these duplicates (ending in "a") is approximately equal to that found in the un-spiked samples. This demonstrates the increase in bacterial activity, and the corresponding increase in sulfate reduction resulting in lower Eh values, higher sulfide concentrations, and thus, more removal of metals that form sulfides. However, it is also possible that

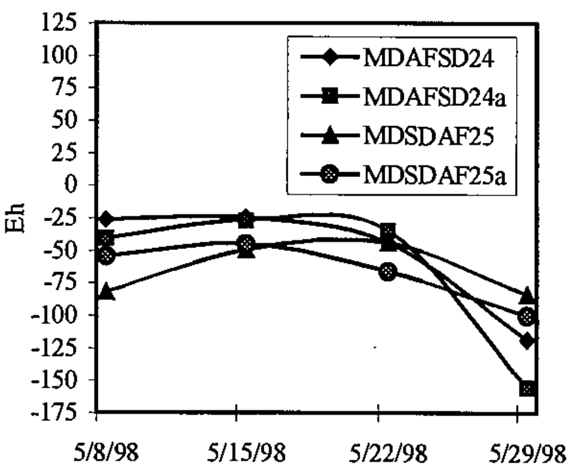

Figure 1. Weekly change in Eh - Anaerobic Tests

TABLE 6. Zinc Removal

Sample	Zn[1]	% Removed[2]
IMDR20	0.995	78%
IMDR20a	0.881	80%
MDDR21	0.388	91%
MDDR21a	0.267	94%
MFDR22	0.276	94%
MFDR22a	0.282	94%
IBDR23	2.655	41%
IBDR23a	1.129	75%
MDAFSD24	0.553	88%
MDAFSD24a	0.192	96%
MDSDAF25	0.229	95%
MDSDAF25a	0.091	98%
SD26	0.109	98%
MD27	0.191	96%
AFSD28	0.226	95%
SDAF29	0.201	96%
SDAFMD30	0.111	98%
AFMD31	0.305	93%
SDMD32	0.082	98%
MDSD33	0.193	96%
SDMF34	0.236	95%
MFSD35	0.220	95%
SDMDU36	0.131	97%
MDSDU37	0.133	97%
SDMFU38	0.272	94%
MFSDU39	0.238	95%

[1]Concentrations in mg/L.
[2]Initial concentration of 4.51 mg/L.

precipitation of gypsum or other sulfate-bearing mineral could have caused the lower S value. One important point to make is that the mixtures (except for maybe IMDR20(a)) did not degrade the water quality significantly. The integrity of the analysis between duplicates, good in most cases, was evaluated by comparing Sr values. The quality of the ICP –AES data seems to be good as evidenced by Sc concentrations close to 1 ppm.

Therefore, considering the aforementioned results, it appears that mixtures 24 and 25 were the best in terms of bacterial growth and metal removal. The results seem to suggest that the bacteria flourish when there is alfalfa present, up to a point. If too much alfalfa is used (samples 28 and 31), the mixture becomes putrid and emits a strong silage odor due to the presence of low molecular weight organic acids. Some of the other mixtures had negative Eh values; however, there appears to be no pattern as to which of the mixtures was superior. In fact, contrary to the hypotheses above, one of the last mixtures on the list

(45% manure), MD 27, proved to be suitable for the growth of bacteria. However, if a treatment system were to contain this much manure, there would most likely be very low flow, if any at all. Therefore, it is important to consider the physical characteristics of the materials in terms of hydraulic conductivity. The next logical step is construction of a small-scale system in order to provide information relating to how well hypotheses concerning hydraulic conductivity will hold true.

Conclusion

Therefore, the results of the experiments allow three important conclusions: 1) The materials at the Belle Eldridge mine site, which include the waste rock and tailings, are not suitable for use in a treatment system. 2) The mixtures that performed the best in the anaerobic experiments were those that contained small amounts of alfalfa, notably samples 24 and 25. Thus, a reasonable substrate composition would be 50% limestone, 25% year-old dairy farm manure, 15% aged sawdust, and 10% alfalfa, all percent by weight. 3) Dairy farm manure (MD) is a good source of anaerobic bacteria.

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