

Bench-Scale Passive Treatment of Heavy Metals Smolnik Mine, Slovakia¹

by

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Abstract: The Smolnik Mine is one of many sources of acid rock drainage (ARD) from inactive mines and mineral processing facilities located in the Ruzin Basin of Slovakia. Drainage from the Ruzin Basin eventually enters the Hornad River contributing to water pollution on an international scale. For centuries, the Smolnik Mine exploited a pyrite deposit. The mine was closed in 1991 after which the underground workings became flooded with ARD containing elevated levels of iron, aluminum, copper and zinc and low pH (2.4). The mine currently discharges ARD into Smolnik Stream at a rate of 18.9 L/sec (300 gpm).

In 1999, bench-scale tests were conducted to evaluate the feasibility of applying passive treatment technology to the Smolnik ARD or other similar local mine water discharges. The test work, tying off research results developed over the past decade, was conducted under a grant from Ecolinks, an arm of the US Agency for International Development (USAID).

Four bench-scale test cells were constructed at the Smolnik mine and operated for two months to provide baseline information to design a larger pilot scale treatment cell. Two of the 200 liter-sized cells treated up to 5 liters of ARD per day. Results showed the viability of sulfate-reducing bacteria and limestone dissolution/exchange to yield metal loading reductions up to 98 percent of the influent values and pH increases to about 5.7. Remarkably, magnesium was removed in all four of the test cells, probably resulting from the formation of iron/magnesium carbonate in reducing redox conditions. The results may provide some clues on the operation of a Successive Alkalinity Producing System (SAPS).

Additional Key Words: Sulfate-reducing bacteria, acid rock drainage, limestone dissolution

Background

The Smolnik Mine is an abandoned underground mine, one of many sources of acid rock drainage (ARD) from inactive mines and mineral processing facilities located in the Ruzin Basin of the

Republic of Slovakia in eastern Europe (Figure 1). Drainage from the Ruzin Basin eventually enters the Hornad River, a tributary of the Danube, contributing to water pollution on an international scale. For centuries, the Smolnik Mine, located about 70 km south of the Polish border with Slovakia, exploited a pyrite deposit; the mine was closed in 1991 after depletion of its economic reserves. By 1994, the underground workings were completely flooded; and the mine started to drain ARD into the adjacent Smolnik Stream. It is well established that water in the presence of pyrite, oxygen, and bacteria becomes acidic (the pH of the Smolnik ARD was initially about 2.4); and this acidic water further dissolves heavy metals from rocks within the mine (Stumm and Morgan, 1981). The concentration of some metals in the ARD entering the Smolnik Stream exceeds the Slovak EPA permissible quality standards by two to three orders of magnitude.

¹ To be presented at the 17th National Meeting of the American Society for Surface Mining and Reclamation, June 11-15, in Tampa, Florida

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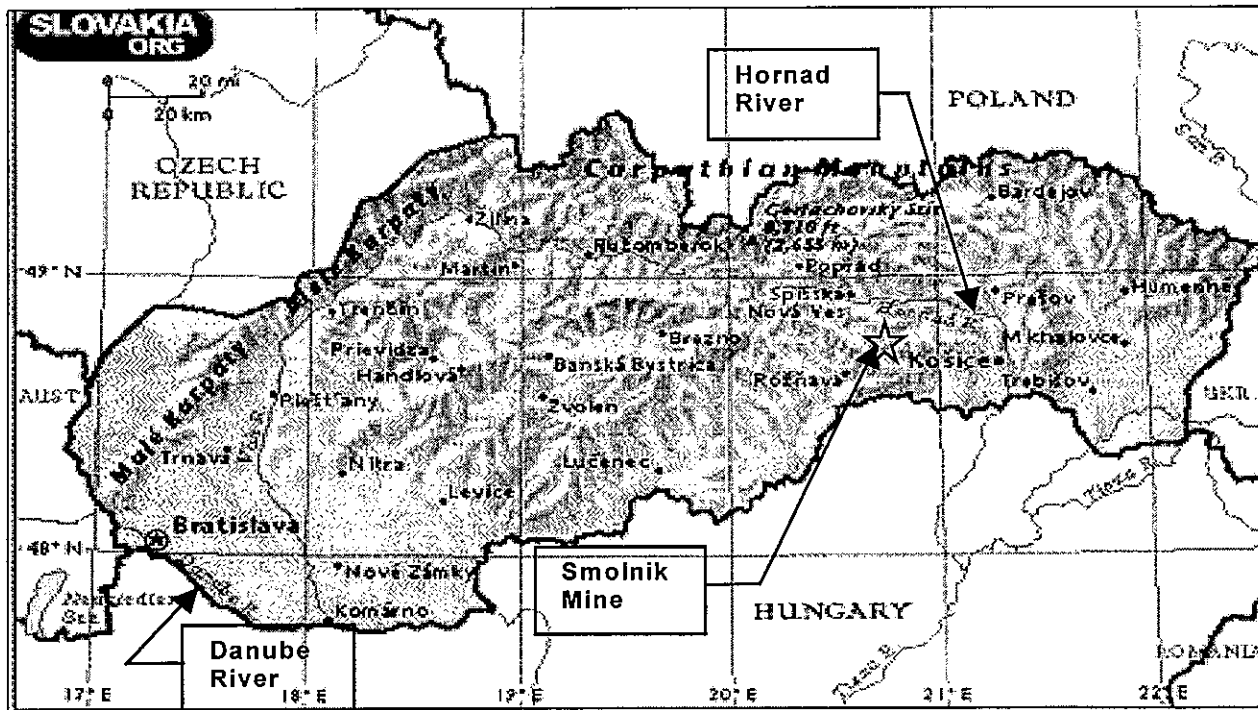


Figure 1. Smolnik Mine Site Vicinity

It is interesting to note that the flooding of the mine may have resulted in some abatement of poor water chemistry conditions that were observed immediately after the mine first started to discharge; further improvements may be possible. As shown in Table 1 below, the water quality parameter values assumed for the design of the tests discussed in this paper are significantly poorer than those actually observed during the test.

Table 1. Design Versus Actual ARD Chemistry

	Test Design Value	Approximate Actual Observed Value
pH	2.4	3.9
Iron	1,500 mg/L	570 mg/L
Aluminum	583 mg/L	120 mg/L
Copper	11 mg/L	3 mg/L
Zinc	62 mg/L	16 mg/L

This situation may be temporary. Long-term monitoring of the mine effluent should reveal if spring snow melt causes the water quality to deteriorate in response to seasonal "flushes" of ARD from the mine rocks. In addition to the parameters of concern in the Smolnik Mine water shown in Table 1 above, other metals are present in minor concentrations. Manganese, while not a focus of the test effort, is present in a concentration of about 40 mg/L.

Project Goals

The objective of the project was to demonstrate that passive treatment can be an effective process in treating the effluent from the Smolnik Mine or similar mining-polluted water. The means to this end included a series of bench-scale tests which would be followed by a pilot-scale test. The project was funded under a grant from Ecolinks, an arm of the U.S. Agency for International Development (USAID). The Smolnik Mine water may be typical of operating metal mines in Slovakia; effective and economical treatment of the water would certainly result in cleaner production practices at operating mines, a key objective of the Ecolinks grant. As such, the project can be viewed as a demonstration of a practical technology in a new situation.

Prior to the commencement of the work, background tests on candidate anaerobic substrate materials were conducted by Dr. Vladimír Sucha of Comenius University, Bratislava, Slovakia. This effort provided a foundation for the test work described herein. The goal of the bench-scale tests was the evaluation of the kinetics of the passive treatment processes for the anaerobic geochemical situation. The following protocols were observed with respect to construction, startup, and monitoring of four bench-scale sulfate-reducing bioreactors.

Anaerobic Cell Setup

Four anaerobic bioreactor cells were constructed on August 5 and 6, 1999, in the Town of Smolnicka Huta about 1 km from the main discharge pipe at the mine. This location was selected for security reasons (to avoid a situation likely to encourage vandalism) and for convenience of the former mine worker who obtained samples of the bench-scale cell effluents and monitored the pH of the cells and other parameters during the test.

Samples of the following cell components were obtained:

- Crushed limestone (4 to 8 mm nominal particle diameter) from a local quarry
- Aged sawdust from a stockpile about 2 km northeast of Smolnicka Huta
- Fresh sawdust from the surface of the stockpile described above
- Moldy hay from a local farmer
- Aged cow manure from the same local farmer

These components were combined in various proportions by as-received weight (i.e., water content included) in four bench-scale cells as shown in Table 2 below. In the case of Cell No. 1, the lower half of the cell has different proportions than the upper part of the cell.

Table 2. Bench-Scale Substrate Proportions in Percent by As-Received Wet Weight

Component	Cell ID				
	Upper ½ No. 1	Lower ½ No. 1	No. 2	No. 3	No. 4
Limestone %	50	20	30	50	30
Old Sawdust %	30	60	30	30	0
Fresh Sawdust %	0	0	0	0	30
Hay %	10	10	30	10	30
Manure %	10	10	10	10	10

The logic behind the selection of the above proportions was based on experience and on general principles on how the substrate has to function to treat the mine drainage (Wildeman and Updegraff, 1998; Gilbert, et al., 1999). Also, it was desired to test the

feasibility of utilizing two different removal mechanisms for iron, which is the most abundant dissolved metal in the Smolnik ARD (Kepler and McCleary), 1994; Watzlaf, 1997). Note that the percentage of manure, the sulfate-reducing bacteria (SRB) inoculum, was held constant for all cells. A description of the logic behind the selection of proportions of each cell follows.

Cell 1. This cell was divided into upper and lower zones with the intent of encouraging removal of iron and aluminum in the upper zone through the dissolution of limestone in a mildly reducing environment, perhaps forming the minerals siderite (FeCO_3) and some aluminosilicate. In the lower zone, SRB were intended to promote the removal of any residual iron plus the copper and zinc as sulfides. The flow in this cell was greater than in the other cells.

Cell 2. This cell had substrate proportions similar to a pilot cell constructed at the Brewer Gold Mine in South Carolina, USA that had similar effluent chemistry derived from a depleted heap leach pad of pyritic gold ore.

Cell 3. This cell had substrate proportions identical to the upper half of Cell 1 and provided a "control" situation in that the flow to this cell was slowly increased over the course of the test to the flow used in Cell 1.

Cell 4. This cell had substrate proportions identical to Cell 2 except that fresh sawdust was substituted for the aged sawdust. Fresh sawdust had been observed in other tests to not be as effective as aged sawdust; fresh sawdust may also be in greater abundance for larger scale construction efforts.

The cells were comprised of 200-liter-capacity plastic trash bins approximately 864 mm high and nominally 533 mm in diameter. A pervious drainage layer consisting of a perforated 2.5-cm-diameter pipe surrounded by limestone gravel (10 mm to 30 mm in diameter) about 40 mm thick was installed in the bottom of each cell (Figures 2 and 3). The pipe penetrated the side of the cell and was connected to a flexible clear plastic hose that rose to the top of the cell. The cells were designed to receive untreated mine water from the top, and the flow direction would be downward. Total substrate weights in the four test cells ranged from 55 kg (Cell 2) to 91.2 kg (Cell 1); Cells 3 and 4 had substrate weights of 82.6 and 66.0 kg, respectively. The void ratio of the substrates varied from 49 percent for Cells 1 and 3 and 61 percent and 67 percent for Cells 2 and 4, respectively. That is,

about 50 percent or more of the volume of a typical cell was filled by void, the balance filled with substrate mass. As the materials in the cell soak up water and/or settle, these values may change.

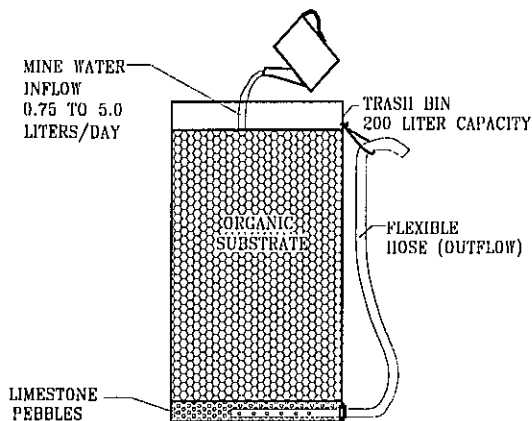


Figure 2. Bench-Scale Anaerobic Test Setup

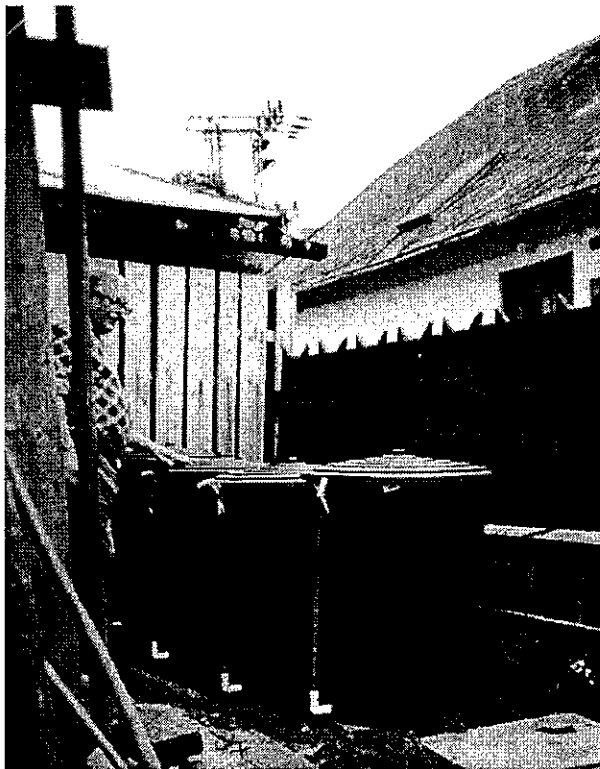


Figure 3. Bench-Scale Test Units

Once the cells were filled with substrate, mine water was added; and the cells were allowed to stand with no flow (incubate) for about a week. Initial geochemical measurements were observed late in the

morning of August 6, 1999. Cell 1 had been filled with Smolnik Mine water less than an hour earlier. The other cells had incubated for about 20 hours. The following measurements shown in Table 3 were observed:

Table 3. Initial Bench-Scale Cell Geochemical Parameters, August 6, 1999, 11:20

Cell ID Component	Untreated				
	Mine Water	No. 1	No. 2	No. 3	No. 4
pH	4.3	4.53	5.79	6.07	5.79
Redox mv)	+229	+159	-240	-90	-50

The pH values in Cells 2, 3, and 4 suggest that neutralization of the mine water acidity had occurred, probably by the dissolution of limestone. There was no evidence of ferric or aluminum hydroxides, which would be indicated by red and white precipitates, respectively. Cells 2, 3, and 4 exhibited some evidence of bacterial activity as suggested by a black, oily-like scum that was seen as a surface sheen. The negative redox values in Table 3 above suggest that reducing conditions (redox less than zero) were established to varying degrees.

Bench Monitoring Parameters and Schedule

The anaerobic cells were monitored for pH, temperature, conductivity, iron, aluminum, copper, zinc, sulfate, calcium, magnesium, smell, and color on a weekly basis. Similarly, the raw Smolnik Mine water was monitored on a weekly basis for a total of five samples that were sent to the Slovak Geological Survey laboratory in Spisska Nova Ves for analysis.

Flows through the cells were non-continuous; a fixed volume of mine water was manually added every day (collected from the mine discharge pipe within one-half hour of addition) to each cell after first removing the same volume of treated water through the flexible hose to prevent overtopping.

The following amounts of mine water, as shown in Table 4, were added to the respective cells every day:

Table 4. Initial Bench-Scale Cell Flow Amounts Beginning August 13, 1999

Cell ID	No. 1	No. 2	No. 3	No. 4
Vol. Added (L/d)	5.0	0.75	1.0	0.75

The cells were kept covered with the loose-fitting plastic tops for the duration of the test. The daily flow in Cell 3 (whose substrate mix is identical to that used in the upper half of Cell 1) was incrementally increased after a month at the initial flow in accordance with the following schedule shown in Table 5:

Table 5. Cell 3 Flow Amounts

Week	1	2	3	4	5
Vol. Added (L/d)	1.0	1.0	1.0	1.0	2.0

Week	6	7	8	9	10
Vol. Added (L/d)	3.0	4.0	5.0	5.0	5.0

The rates specified for Cells 2 and 4 were selected on the premise that sulfate reduction would be the primary metal removal mechanism (based on the presumed water quality provided in Table 1). Cells 1 and 3 received water at a rate to induce limestone dissolution and/or sulfate reduction.

Test Results

Metal Removal Performance and pH Improvement

The performance of the four bench-scale test cells were monitored on a weekly schedule since their commissioning on August 19, 1999. Figures 4 and 5 below compare quality of the raw mine water (influent) and the discharge (effluent) from the four test cells.

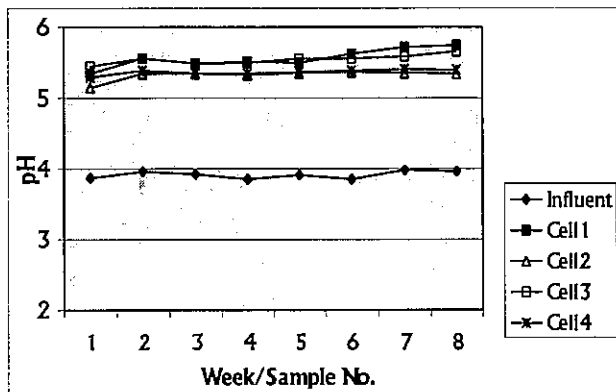


Figure 4. Smolnik Bench Test Results - pH

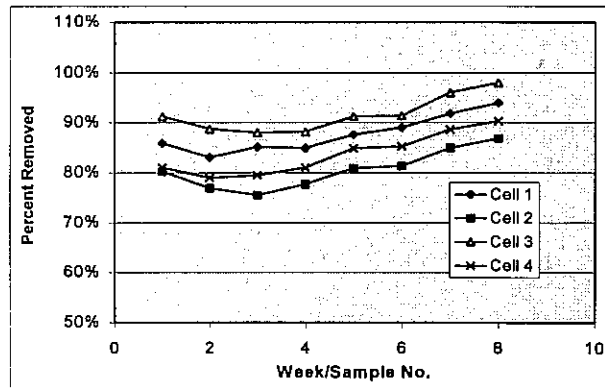


Figure 5. Combined Metals Removal Iron, Aluminum, Copper, and Zinc

The data show that all four cells were successful at metals removal, especially those with higher amounts of limestone in their substrate mix (Cells 1 and 3). The pH values also improved more for Cells 1 and 3 compared to Cells 2 and 4. As expected, manganese removal overall was poor, which is typical of the anaerobic type of treatment cell. Influent manganese concentrations averaged about 38 mg/L; effluent concentrations at week 8 averaged about 26 mg/L for all four cells.

Table 6 provides a direct comparison of all cells and all metals removal.

Table 6. Combined Metals Removal (moles/day/m³) Fe, Al x 1.5, Cu, Zn

Date '99	Feed 1	Effl. 1	% Rem	Feed 2	Effl. 2	% Rem
8/19	0.44	0.06	86%	0.08	0.02	80%
8/26	0.43	0.07	83%	0.08	0.02	77%
9/2	0.43	0.06	85%	0.08	0.02	76%
9/9	0.43	0.07	85%	0.08	0.02	78%
9/16	0.49	0.06	88%	0.09	0.02	81%
9/23	0.48	0.05	89%	0.08	0.02	81%
10/1	0.50	0.04	92%	0.09	0.01	85%
10/7	0.51	0.08	94%	0.09	0.01	87%

Date '99	Feed 3	Effl. 3	% Rem	Feed 4	Effl. 4	% Rem
8/19	0.08	0.01	91%	0.07	0.01	81%
8/26	0.08	0.01	89%	0.06	0.01	79%
9/2	0.08	0.01	88%	0.06	0.01	80%
9/9	0.08	0.01	88%	0.06	0.01	81%
9/16	0.18	0.02	91%	0.07	0.01	85%
9/23	0.26	0.02	91%	0.07	0.01	85%
10/1	0.36	0.01	96%	0.07	0.01	89%
10/7	0.45	0.01	98%	0.08	0.01	90%

The data above show the unit mass loading (moles/day/m³) of metals (Fe, Al x 1.5, Cu, and Zn) in

the feed water compared with the unit mass loading rate of metals contained in the respective effluents followed by the percent removed. All cells show improvements as the test progressed, but these results can be interpreted further. Compare the unit mass loading feed rates of Cells 1 and 3 for the sampling date of October 7, 1999, with the values for Cells 2 and 4 on the same date. The higher the value (0.51 or 0.45 [feed 1 & 3] compared to 0.09 or 0.08 [feed 2 & 4]), the higher the "efficiency" of the cell for a similar metal removal percentage.

Note that the moles of aluminum are increased by 50 percent in the table above due to the effect of the ionic charge of aluminum (+3) compared to the ionic charges for iron, copper, and zinc (+2). By accounting for the different ionic charges, the unit mass loading rate values for metals can be directly compared with the unit mass sulfate removal rates in Table 7 that follows.

Table 7. Sulfate Reduction (moles/day/m³)

Dates	Cell 1	Cell 2	Cell 3	Cell 4
'99				
8/19	0.39	0.04	0.10	0.05
8/26	0.43	0.07	0.13	0.08
9/2	0.25	0.03	0.08	0.03
9/9	0.28	0.06	0.10	0.05
9/16	0.26	0.06	0.21	0.07
9/23	0.32	0.07	0.38	0.08
10/1	0.40	0.08	0.47	0.08
10/7	0.43	0.09	0.47	0.08

In passive treatment cells that utilize sulfate reduction as the prime metal immobilization method, the unit mass loading rates for metals are typically matched with the unit mass reduction rate for sulfate. Comparing the date-respective values on the previous two tables reveals close agreement between metal removal and sulfate reduction unit rates. Thus, the two processes (metal precipitation and sulfate reduction) appear to be evenly matched for all four test cells. More importantly, the data again show that Cells 1 and 3 are outperforming Cells 2 and 4. A "benchmark" sulfate reduction rate observed at other mine sites where SRB passive treatment cells have been installed is 0.3 moles/day/m³ of organic substrate. Cell 1 appears to be reaching and exceeding this benchmark value, almost from startup. Cell 3 appears to do the same as the flows were increased from 1 L/day (first four samples) to 5 L/day (last four samples).

These data further suggest that sulfate reduction is the predominant removal mechanism since the metals removed are nearly equal to the sulfate

reduced. This is an important design consideration for scaling up to a pilot-sized cell.

If the combined metal removal rates (feed moles minus effluent moles) per day per cubic meter of substrate are compared among all four cells, Cell 1 is performing the best with Cell 3 performing nearly as well. This might be expected due to the similar proportions of substrate components in these two cells. The removal rates on a percentage basis are better in Cell 3 than Cell 1 initially, but this is to be expected due to the lesser amount of mine water that Cell 3 was required to treat (1 L/day) compared to Cell 1 (5 L/day). In summary, the Cell 1 substrate configuration (upper half, 50 percent limestone; lower half, 20 percent limestone) yielded the best consistent results. Metals removal was consistently greater than 85 percent of the amount fed to the cell.

Limestone Consumption

The initial design of the test cells presumed that limestone dissolution would be the predominant mechanism of raising pH and thereby precipitating aluminum and removing iron as a substitution for calcium in the limestone matrix to form the iron carbonate mineral siderite. To evaluate this mechanism, calcium and magnesium concentrations in the influent and effluent to each cell were monitored. Limestone typically contains both calcium and magnesium, so analyses for both of these cations would provide a quality assurance check on limestone dissolution rates.

Furthermore, if siderite were indeed forming, then the increase of calcium and magnesium in the effluent would closely match the decrease in iron that was unaccounted for by sulfate reduction. As stated previously, it appears that all metals are being removed as sulfides. As shown in Table 8 below, calcium was indeed liberated, which supports the dissolution of limestone in all four cells.

Table 8. Calcium Concentration Gains (ppm) Indicating Limestone Dissolution

Date	Influent	Cell 1	Cell 2	Cell 3	Cell 4
'99					
8/19	215	745	734	798	818
8/26	238	849	874	882	923
9/2	209	736	826	805	900
9/9	211	754	833	794	918
9/16	208	665	776	705	897
9/23	211	560	794	741	915
10/1	215	567	792	659	925
10/7	218	460	798	599	921

However, as Table 9 below shows, magnesium was anomalously consumed in all four test cells. This was completely unexpected but is consistent within the context of an assumed dominance of sulfate reduction as the primary metal removal mechanism.

Table 9. Magnesium Losses (ppm) Suggesting Dolomite Formation

Date '99	Influent	Cell 1	Cell 2	Cell 3	Cell 4
8/19	410	231	281	228	282
8/26	410	260	293	248	282
9/2	375	249	280	235	272
9/9	373	264	269	243	269
9/16	366	262	256	230	265
9/23	370	250	261	229	265
10/1	381	260	257	236	267
10/7	387	251	262	241	261

It is suspected that a substitution of magnesium for calcium was occurring in the limestone, resulting in the formation of the mineral dolomite or some other mixed-metal carbonate. As shown in Tables 10 and 11, the stoichiometric replacement of calcium by magnesium was not perfect on a mole-for-mole basis, which might be expected if calcium carbonate was fully dissolved to assist the SRB in raising the pH of the effluent. This can especially be seen in Cell 1, which had the highest flow. Calcium dissolution is high, initially at 0.066 moles per day, decreasing to 0.03 moles per day as Cell 1 matured and perhaps the SRB component of pH mitigation became more dominant. Calcium dissolution in the other cells was not as pronounced with the exception of Cell 3 in the last four weeks of sampling when flows to that particular cell were increasing at a rate of a liter per day per week.

Table 10. Limestone Dissolution/Replacement, Moles/Day or Calcium Displacement, Moles/Day

Dates '99	Cell 1	Cell 2	Cell 3	Cell 4
8/19	0.066	0.010	0.015	0.011
8/26	0.076	0.012	0.016	0.013
9/2	0.066	0.012	0.015	0.013
9/9	0.068	0.012	0.015	0.013
9/16	0.057	0.011	0.025	0.013
9/23	0.044	0.011	0.040	0.013
10/1	0.044	0.011	0.044	0.013
10/7	0.030	0.011	0.048	0.013

The limestone dissolution history described above is also reflected in Table 11 below.

Table 11. Magnesium Decrease, Moles/Day

Dates '99	Cell 1	Cell 2	Cell 3	Cell 4
8/19	0.037	0.004	0.007	0.004
8/26	0.031	0.004	0.007	0.004
9/2	0.026	0.003	0.006	0.003
9/9	0.022	0.003	0.005	0.003
9/16	0.021	0.003	0.011	0.003
9/23	0.025	0.003	0.017	0.003
10/1	0.025	0.004	0.024	0.004
10/7	0.028	0.004	0.030	0.004

If the dissolution and flow rates observed on the October 7, 1999, sampling date are assumed, the limestone mass contained in the cells will be consumed or transformed to dolomite in 24 to 42 years. Experience has shown that organic matter in SRB cells is typically consumed in about the same period. Thus, the data suggest that the longevity of this particular cell substrate would be on the order of two decades before it would require replacement. This is well within the approximate time frame to qualify the treatment methodology as truly "passive."

Comparison of the Test Results to the Behavior of SAPS Units

The data above provide an interesting comparison to what is observed in a typical Successive Alkalinity Producing System (SAPS) that is dominated by limestone dissolution. In the original report by Kepler and McCleary (1994), limestone dissolution was cited as accounting for the majority of the alkalinity production in the three SAPS systems investigated. In all three cases, studies lasted for more than one year. In the compost/limestone downflow columns that Watzlaf (1997) investigated, sulfate reduction contributed about one-third of the alkalinity produced in the beginning and that decreased to less than 10 percent by the end of the first year. In both of these studies, the top layer was mushroom compost that contains 10 percent limestone; and the bottom layer is 100 percent limestone. In the bench-scale cells in this study, there is not a pure limestone layer at the bottom; and the ratio of limestone to organic material is much higher than in mushroom compost. In the Watzlaf (1997) study, sulfate reduction diminished because the pH in the upper compost layer dropped to below 5. It may be that if these bench-scale studies were continued for over a year that a similar pH drop would be seen, and sulfate reduction would be diminished if the limestone was totally consumed.

In the two previous studies, the concentrations of calcium increased and iron decreased. Removal appears to have been by the formation of siderite. In this study, the increase in calcium is almost balanced by the decrease in magnesium; and little iron appears to be removed by the formation of siderite. It should be noted that the concentration of magnesium in this mine drainage is higher than what is usually encountered. It is not clear why these bench-scale systems operate as sulfate-reducing systems even though an effort was made to try to remove iron through the formation of siderite. It may be that the concentration mix of cations in the water (such as Mg, Ca, Fe, Zn, and Mn) that can form insoluble carbonates dictates what metals will be removed when limestone dissolves. If this is the case, then these anoxic limestone systems exhibit a very efficient use of the carbonate alkalinity that is present to cause precipitation of the most favorable carbonate.

Preliminary Pilot Cell Design Recommendations

As previously stated, the performance of Cell 1 appeared to provide the best overall removal among the four test cells with Cell 3 ranking slightly behind. However, the two designs are similar with the exception that Cell 3 has more limestone. Since limestone dissolution appears to be important only during startup as evidenced by the falling dissolution rates over time, the sulfate-reducing component of the cell's "fuel" supply should be given greater mass. That is, the configuration of Cell 1 with its multi-layer approach is superior to the monolithic substrate mass of Cell 3.

General Summary/Recommendations

Based on the sulfate reduction values and the concentration of metals in the effluent water samples, sulfate reduction appeared to work well in all four cells with some supporting dissolution of limestone. The substrate mixtures with the highest limestone proportions (Cells 1 and 3) appeared to perform well under the stress of low pH values in the feed water. The Cell 1 design was deemed the best for scale-up to pilot size.

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