REMEDIATION OF ACID MINE DRAINAGE WITHIN STRIP MINE SPOIL BY SULFATE REDUCTION USING WASTE ORGANIC MATTER [1]

Jeralee Stalker, Arthur W. Rose and Louise H. Michaud[2]

Abstract: Many treatment options for AMD, like wetlands and anoxic limestone drains, are limited by acidity, metal loadings, flow rate or areal requirements so as to be inapplicable at many sites. *In-situ* bacterial sulfate reduction is proposed as a solution for certain settings. Requirements for successful *in-situ* bacterial sulfate reduction include dissolved sulfate, an organic substrate, permanent anaerobic conditions, a mixed culture of bacteria, appropriate nutrients, and a sufficient AMD contact time. These requirements can be provided within mine spoil by injection of waste organic matter into an extensive zone of saturated spoil.

Laboratory experiments on cheese whey, lactate, non-degraded sawdust, partially degraded sawdust, pulped newspaper and mushroom compost have all yielded sulfate reduction, increased alkalinity and iron sulfide precipitate in AMD with $pH < 4.0$. The addition of a small amount of dolomite to the organic matter creates alkaline microenvironments that facilitate the initiation of sulfate reduction. The rates of sulfate reduction using cellulose materials are slow but the rate for milk products is much more rapid.

A field test utilizing partially degraded sawdust is underway. A total of 11.3 tons of sawdust mixed with 5% dolomite, 5% sewage sludge and a mixed bacterial culture was successfully injected into 4 drill holes in mine spoil as 13% w/v suspension. The spoil had enough coarse porosity for injection into the saturated subsurface at about 300 L/min. Data on *in-situ* SO_4 reduction rates and water quality are being collected in preparation for a full remediation program at the site, which has an extensive zone of saturated spoil 10-20 m thick.

Additional Key Words: acid mine drainage, sulfate reduction, *in-situ* remediation, organic addition

Introduction

Although generation of acid mine drainage (AMD) at new surface coal mines has been largely eliminated by changes in federal and state regulations, many previously mined sites release severe AMD that contaminates streams in western Pennsylvania and other coal mining areas. "Passive" methods such as wetlands, compost wetlands, anoxic limestone drains (ALD) and alkalinity producing systems (APS) are beginning to provide methods for treating these AMD flows (Hedin et al., 1994). However, aerobic wetlands satisfactorily mitigate only AMD containing net alkalinity. Weltands also require a large area and become less effective in cold weather. ALD's can neutralize a maximum of only about 250 mg/l acidity, and require considerable area and length for large flows, as do compost wetlands and APS. This paper describes the injection of waste organic matter into strip mine spoil to promote bacterial sulfate reduction as an additional passive method. Figure 1 schematically illustrates a situation in which *in-situ* sulfate reduction may perform satisfactorily.

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[2] Jeralee Stalker, Graduate Assistant and Arthur W. Rose, Professor of Geochemistry Department of Geosciences; and Louise H. Michaud Assistant Professor of Mining Engineering, Department of Mineral Engineering.
Pennsylvania State University., University Park, PA, 16802 USA.

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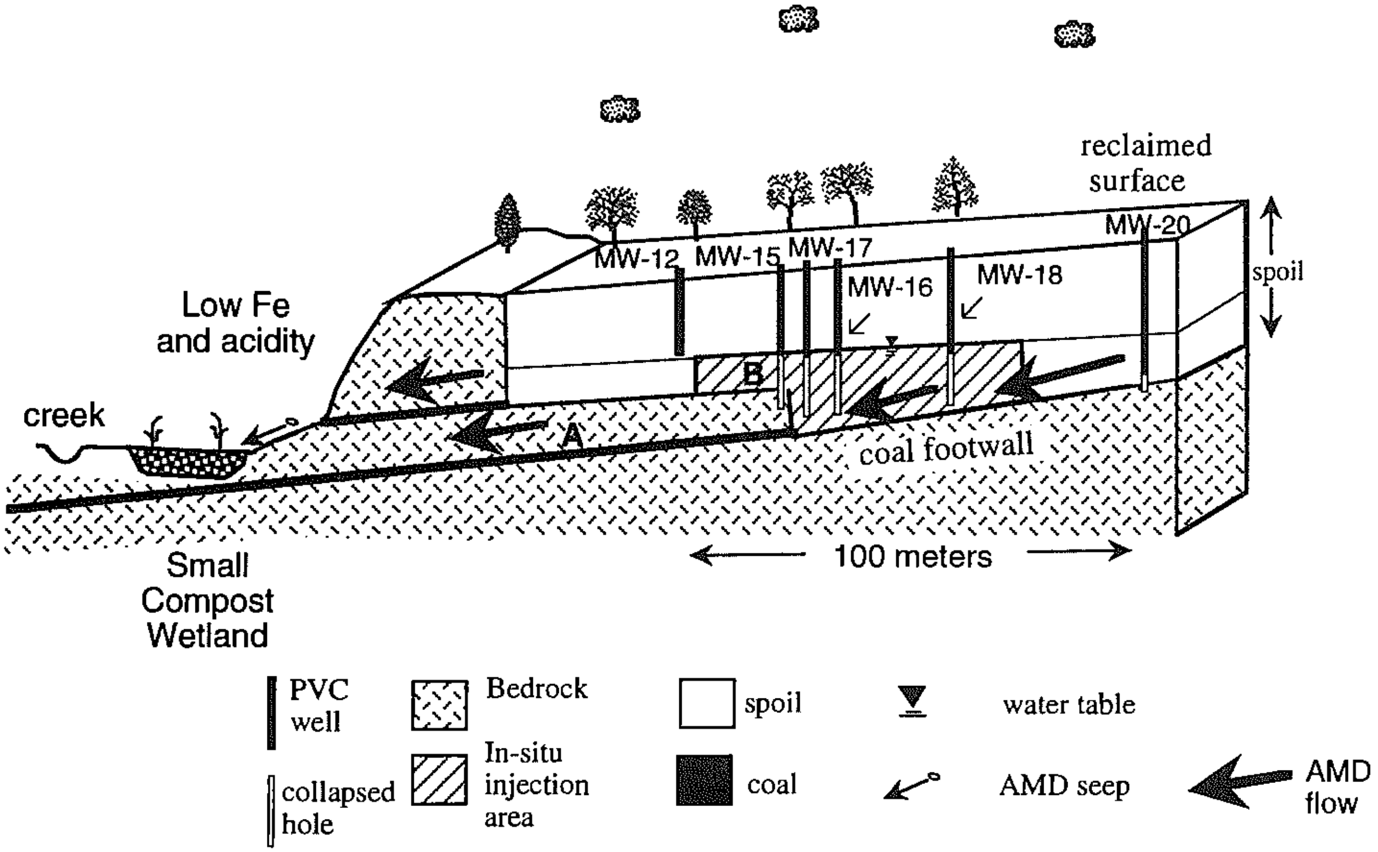

Figure 1. Schematic diagram of the area of in-situ sulfate reduction. Wells at the site are indicated. A hypothetical wetland is included in the diagram. Thick arrows indicate possible ground water flow paths. A) AMD may flow between the Mercer and Brookville coals in a sandstone unit and emerge as seeps along the crop line. B) This may be an area of little flow. Due to the shallow water table in this area, anaerobic conditions may not be maintained here.

To investigate the applicability of *in-situ* sulfate reduction, laboratory experiments were conducted on several waste organic materials to determine rates of sulfate reduction and to investigate limitations on the process, such as pH. Based on successful results of the laboratory experiments, a field test at a reclaimed strip mine was designed and implemented, and is being monitored.

Sulfate Reduction

Sulfate reduction is accomplished by several species of bacteria that obtain metabolic energy by reacting sulfate with simple organic compounds such as lactate, pyruvate, ethanol or acetate (Brock et al, 1994). They require an O_2-free environment because aerobic bacteria deplete the levels of these organic substrates to levels too low for utilization by sulfate reducing bacteria (SRB). In general, the SRB produce H_2S (or HS^-) and alkalinity (HCO_3^-). The H_2S reacts with dissolved Fe to precipitate FeS or a similar compound.

SRB cannot break down complex organic substrates; they rely on other bacteria, mainly fermenting bacteria, to provide substrates like acetate and lactate from larger organic molecules such as glucose or cellulose (Chapelle, 1993).

An example of the reaction accomplished by SRB on a lactate substrate at slightly acid pH (4 to 4.5) follows:

$$SO_4^{2-} + 2CH_3CHOHCOO^- + 4H^+ = H_2S + 2CH_3COOH + 2H_2CO_3 \quad (1)$$

Given the pK's for dissociation of lactic acid (3.8), acetic acid (4.75) and carbonic acid (6.5), the nature of the products depends on pH. At alkaline pH (pH>6.5), the products would be acetate (CH_3COO^-) and HCO_3^-, and no H^+ would be consumed but alkalinity would be produced. Some SRB are able to utilize acetate to reduce sulfate (Brock et al., 1994):

$$SO_4^{2-} + CH_3COO^- + 3H^+ = H_2S + 2H_2CO_3 \quad (2)$$

The total oxidation of lactate by sulfate is thus:

$$3SO_4^{2-} + 2CH_3CHOHCOO^- + 8H^+ = 3H_2S + 6H_2CO_3 \quad (3)$$

If H_2S does not degas or complex with other species, it can dissociate to HS^- and/or react with dissolved Fe^{2+} to precipitate FeS:

$$H_2S = H^+ + HS^- \quad (pK = 7.0 \text{ at } 25°C) \quad (4)$$

$$Fe^{2+} + HS^- = FeS + H^+ \quad (5)$$

An overall reaction generating FeS from SO_4 and lactate at pH 4.75 to 6.5 is:

$$3SO_4^{2-} + 2CH_3CHOHCOO^- + 3Fe^{2+} + 2H^+ = 3FeS + 6H_2CO_3 \quad (6)$$

Under certain conditions, sulfate reduction has the capability of producing pyrite from AMD, though the reaction is generally slow compared to FeS precipitation. In fact, bacterial sulfate reduction during sedimentary diagenesis was responsible for the formation most of the original pyrite in the rocks that produce AMD. Pyrite has been observed in several AMD localities undergoing sulfate reduction (Hedin et al., 1988).

In contrast to anoxic limestone drains, sulfate reduction is not limited in the amount of alkalinity that can be produced by SRB. The main limitations are the rate of the process, which may be relatively slow, especially if fermentative bacteria are necessary to break down cellulose or other complex organic compounds to simpler coumpounds metabolizable by

SRB. The pH may also be a limitation, since SRB prefer pH values above 5 (Zajic, 1969).

Materials and Methods-Laboratory Study

Prior to the *in-situ* test of sulfate reduction at the Pot Ridge mine, several organic substrates were tested in the laboratory. Initial substrate selection was based on a combination of characteristics including availability, cost, longevity and previous work indicating ability of SRB to degrade the substrate. Tuttle et al, (1969a, 1969b) showed that flow of AMD through a sawdust pile accomplished some remediation, and that cellulose could reduce SO_4 in lab experiments. Compost wetlands and APS accomplish some of their effect by sulfate reduction. Composted organic matter, hay, spent mushroom compost and other inexpensive organic materials have been used as organic substrates for sulfate reduction (Bechard et al., 1994, Bechard et al., 1995, Eger and Wagner, 1995, Dvorak et al., 1991, McIntire et al., 1990, Hammack and Edenborn, 1992, Borek et al., 1995). Waste whey from cheese production was initially tested as a substrate. Later substrates tested included fresh and degraded sawdust, newspaper, and spent mushroom compost.

In initial experiments with sawdust and pH 3.85 AMD, sulfate reduction had not started at day 217, but addition of 10% by weight dolomite led to fluctuating decreases in sulfate in 6 days and sustained decreases in sulfate in about 50 days. The dolomite particles apparently furnished alkaline microenvironments in which the bacteria could thrive. Therefore, dolomite particles (100 mesh) or alkaline fly ash was added to later experiments.

Intial experiments also indicated that low redox conditions are absolutely necessary to stimulate sulfate reduction. Several types of plastic tubing were used in systems for circulating AMD through substrate-filled columns, but all were found to be permeable to O_2 , resulting in Fe-oxide precipitation and slow to negligible sulfate reduction. The most useful data was obtained in glass systems completely closed to air except during brief addition of fresh AMD.

Bacteria from waste water at the Penn State Sewage Treatment Plant were initially cultured with cheese whey and an $FeSO_4$ solution. After sulfate reduction was observed in this medium, the culture was divided into several closed containers and fed lactate and $FeSO_4$ periodically. Later experiments were inoculated with 10 ml of this culture.

The lactate and whey experiment included 1 liter of synthetic AMD ($FeSO_4 \cdot 7H_2O$) and whey initially, then reagent grade calcium lactate. This experiment was circulated through a flask filled with glass beads (Figure 2A) by bubbling a constant stream of ultra high purity (UHP) N_2 through tubing connecting the bottom and top of the column. Samples were collected weekly from one of the top openings under a stream of UHP N_2 using a pipet.

The experiments with solid substrates were run in glass ion chromatography columns (2.2 cm diam x 50 cm length) (Figure 2B) with 125 mL of AMD from the Pot Ridge site and variable amounts of substrate (Table 1). Sawdust, spent mushroom compost and newspaper were tested. Table 1 indicates the organic substrates tested, the alkaline material added to the experiment, the volume of organic substrate added and the initial sulfate concentrations. Weekly, 20 ml was drained from the bottom and analyzed, and 20 ml of fresh AMD was added to the top of the columns.

The pH, Eh, and temperature were measured *in-situ* for the lactate experiment and immediately after the effluent was drained from the columns for the solid substrates. Alkalinity

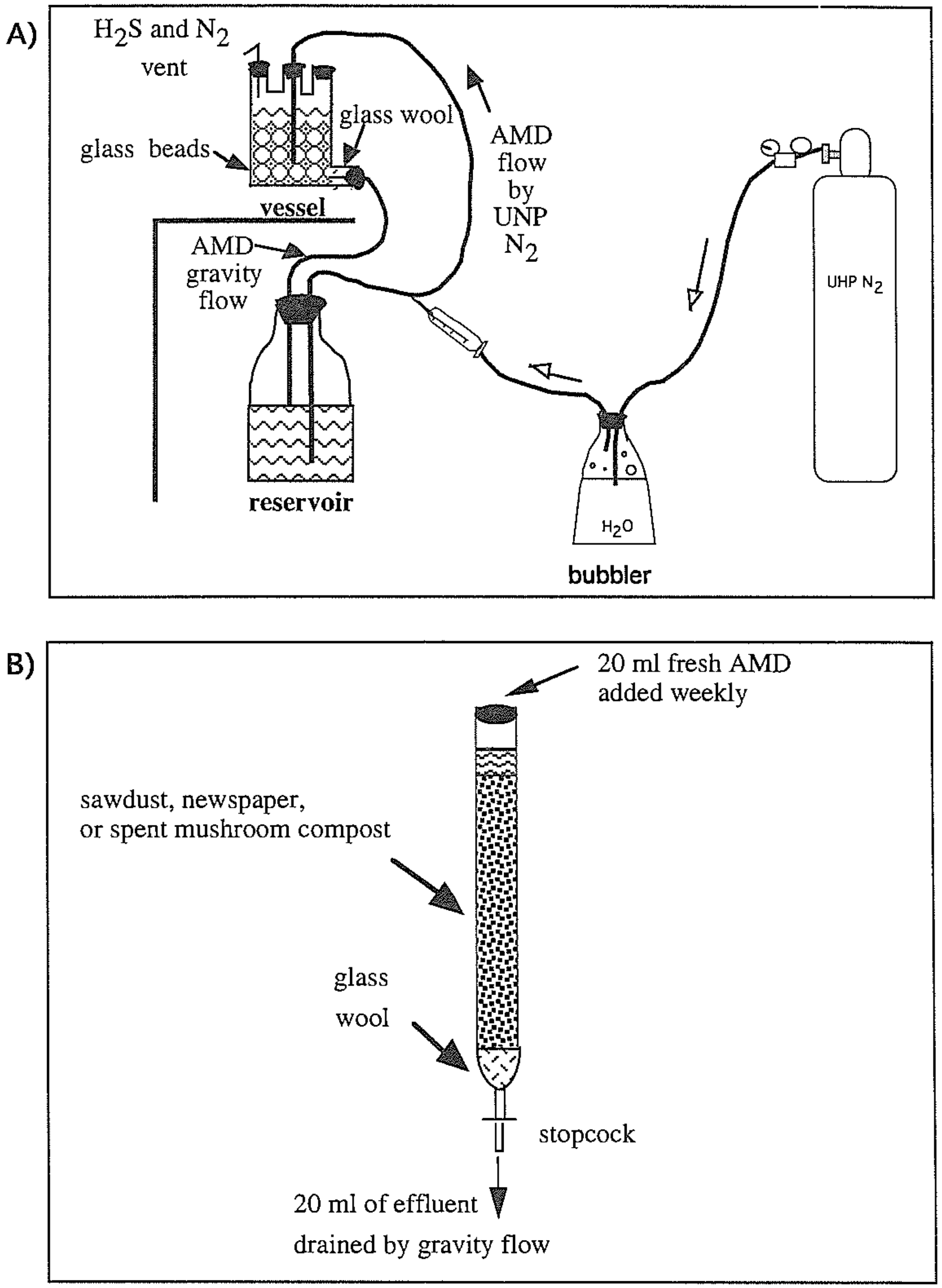

Figure 2. A) Reaction vessel and reservoir . B) Column design. Weekly, 20 ml of effluent was drained from the stopcock and fresh AMD was replaced at the top.

Table 1. Organic substrates, alkaline and AMD sources for each experiment.

Organic substrate	Alkaline source	Amount of Substrate	SO_4 mg/L	AMD source and amount
Fresh sawdust	FBC fly ash (10%)	3.84 cm^3	641 mg/L	150 ml AMD
Degraded sawdust	FBC fly ash (10%)	24.05 cm^3	641 mg/L	150 ml AMD
Spent mushroom compost	limestone	22.65 cm^3	641 mg/L	125 ml AMD
Newspaper	dolomite	5.37 cm^3	641 mg/L	125 ml AMD
Lactate	------	2400 mg/L	1585 mg/L	1L $FeSO_4$

was determined immediately after sampling and was followed by hot acidity. Methods are summarized in Table 2. Samples were diluted for ICP analysis using a ratio of 6 ml sample: 1 ml concentrated HCl: 23 ml distilled deionized water. All samples were filtered through a .45 micron filter directly after dilution and prior to chemical analysis by ICP.

Results of Laboratory Studies

In general, sulfate reduction was observed for all substrates after varying lag periods. For example, Figure 3 illustrates the behavior of SO_4, Fe and pH in the experiment using lactate. Initially, the low pH solution and high redox conditions inhibit sulfate-reducing bacteria. In a system closed to the atmosphere, O_2 is utilized rapidly by aerobic organisms, lowering the Eh. Fermentation then breaks down the complex organics matter into simpler substrates. Sulfate reducing bacteria utilize the simple organics via equation 6 or a similar reaction involving simple organic matter and sulfate. The bacteria thus create alkaline microenvironments within low pH AMD. Figure 4 summarizes results in the form of percent gains and losses for SO_4 and Fe for each substrate normalized for changing influent concentrations and different

Table 2. Analytical Methods

Method	Procedure
Alkalinity	Method 410 (Fishman and Friedman, 1989)
Acidity	Method 305.1 of E.P.A. (1979) using boiling and H_2O_2 to oxidize Fe
pH	Combination Ag/AgCl electrode standardized with pH 4 and 7 buffers connected to an Orion 205A or a Fisher Scientific Accumet pH Meter
Eh	platinum electrode with an Ag/AgCl reference electrode
Mn, Al, Fe,S Ca, Mg, Na, K	Plasma Spectrometry (ICP)

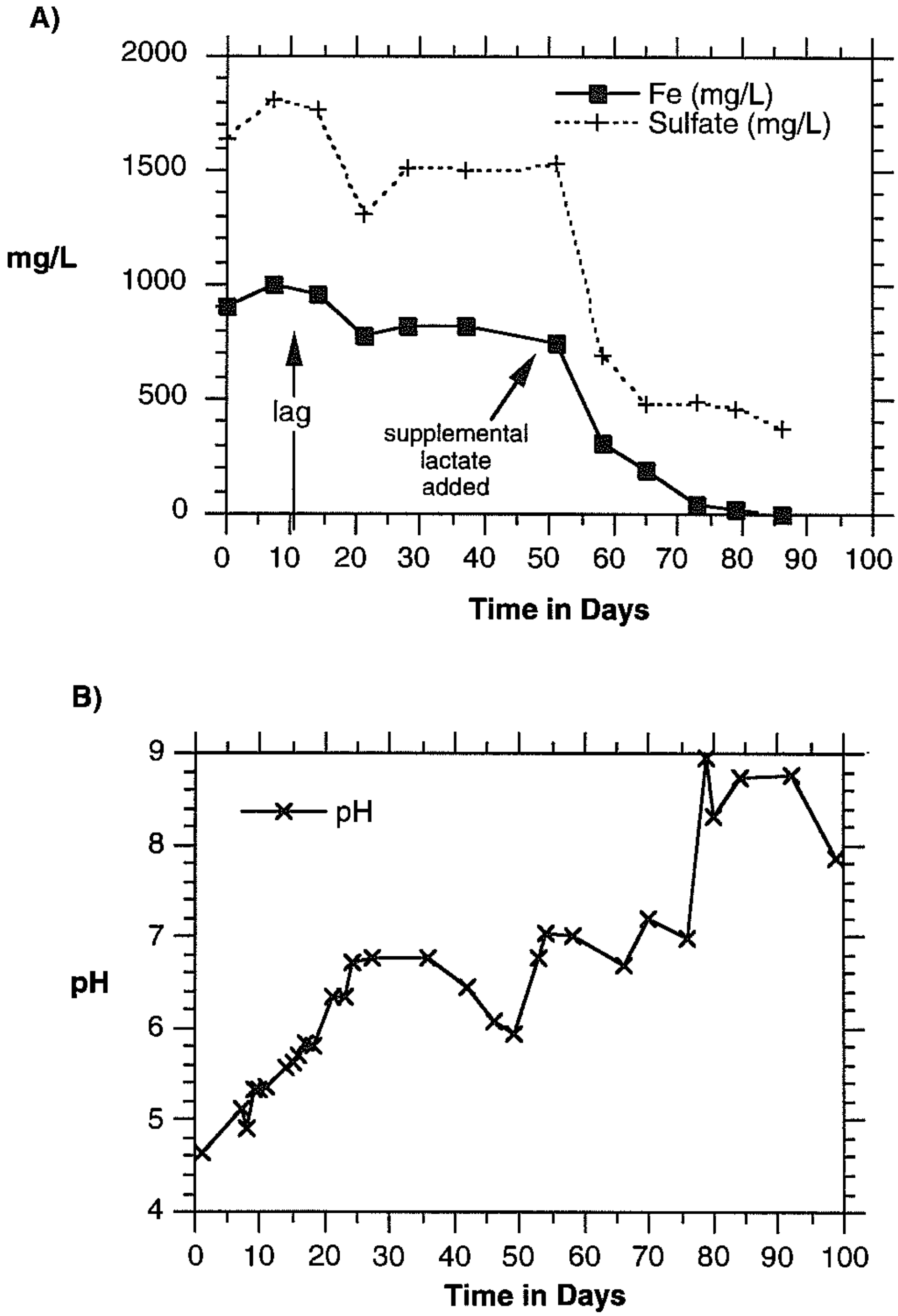

Figure 3. Plot of sulfate, iron (A) and pH trends (B) over time for the lactate experiment as an example of the raw data. The lag time before sulfate reduction is between day 0 and day 15. Sulfate decreases rapidly after this period. The ceasing of sulfate reduction from day 30 to day 55 represents a period of negligible organic matter concentrations. Sulfate decreases again when lactate is added on day 46.

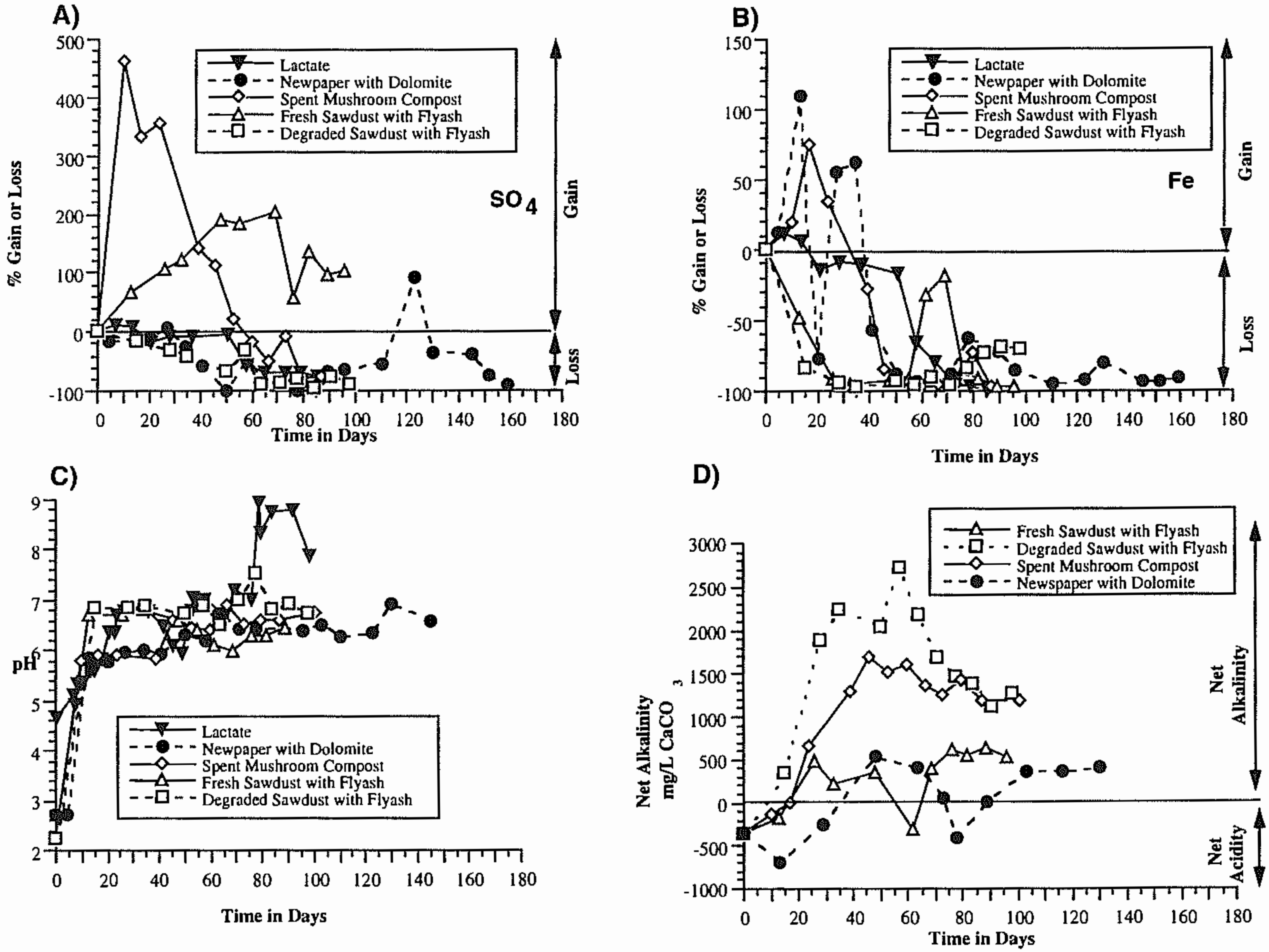

Figure 4. Experimental data for various organic substrates tested in the lab. A) and B) Gains and losses for sulfate and iron are expressed in % relative to the influent concentrations; C) pH over time; D) Net alkalinity over time.

substrate volumes. The influent concentrations of Fe and SO_4 for the lactate experiment were 870 mg/L and 1585 mg/L respectively. For the other experiments which used solid substrates, the influent concentrations of Fe and SO_4 were 38 mg/L and 641 mg/l respectively.

Several experiments showed increases in sulfate and other solutes during an early leaching period. An increase in SO_4 was observed in the mushroom compost due to the dissolution of gypsum and in the fresh sawdust amended with fly ash due to the leaching of sulfate from the fly ash. No excess sulfate was observed for the degraded sawdust with fly ash; however, cation concentrations for Ca, Mg, K and Na increased in both substrates suggesting that these constituents were being leached from fly ash in both degraded and fresh sawdust substrates. The cation leaching period lasted for the entire length of the experiment for both sawdust substrates. Although some leaching of Fe is indicated in Figure 4 for the newspaper with dolomite and the spent mushroom compost, nearly 100% of the Fe was removed in all experiments to once sulfate reduction began. Erratic patterns for some substrates may be due to disturbance of the anaerobic environment.

Average sulfate reduction rates were calculated for each of the column experiments using the decrease in sulfate concentrations over time per gram of substrate (Table 3). Rates were calculated for the lactate experiment using the decrease in sulfate concentrations over time per liter of AMD. Gypsum dissolution in the sawdust experiments that contained fly ash yielded excess SO_4 in these columns. In order to obtain sulfate reduction rates that reflected this additional SO_4 concentration, the analytical data was corrected using the molar ratio of $Ca:SO_4$ from control experiments (Stalker, 1996). The sulfate reduction rates for fresh and degraded sawdust were calculated using corrected SO_4 values. The sulfate reduction rates obtained for the degraded sawdust with fly ash experiment are probably underestimated, as both the sulfate leached from fly ash and the sulfate in influent AMD are reduced. Rates of sulfate reduction for the mushroom compost and newspaper with dolomite experiments were determined during the later portion of the experiments, after leaching. The alkalinity and pH trends over time indicate that all experiments went from acidic to near neutral pH levels with a concomitant rise in alkalinity (Figure 4). Alkalinity was not measured during the course of the lactate experiment, but a net alkalinity of 260 mg/l $CaCO_3$ was measured at the culmination of the experiment.

All experiments produced effluents with high alkalinity. However, since some alkalinity could be furnished by carbonate dissolution or consumed by precipitation of Fe and Al hydroxides, the source of alkalinity deserves consideration. Based on the increased Ca and decreased SO_4 in solution, dissolution of added dolomite, and alkaline components of fly ash and mushroom compost is estimated to contribute 70-

Table 3. Calculated sulfate reduction rates for the experimental organic substrates.

Substrate	**Average SO_4 Reduction Rate**
Lactate	197 mmol/L/day
Newspaper with dolomite	69 nmol/g/day
Spent Mushroom Compost	60 nmol/g/day
Fresh sawdust with fly ash	20 nmol/g/day
Degraded sawdust with fly ash	148 nmol/g/day

90% of the alkalinity, especially during the early stages of the experiment. However, some alkalinity was attributable to sulfate reduction in each experiment.

Site of the Field Test

The Pot Ridge mine located near Dunlo, PA, U.S.A. was the focus of the field study. The mine is a 198.3 hectare strip mine that was reclaimed approximately 10 years ago. Forty-four highly acidic AMD seeps emerge near the cropline of the Brookville coal and flow into nearby Paint Creek.

In the central part of the Pot Ridge mine, ground water is ponded against an internal highwall bounding an up dip zone where the deeper Mercer coal as well as the Brookville and Clarion coals were mined (Figure 1), and a down dip mine where only the upper two coals were mined (Figure 1). A saturated zone up to 13 m thick is ponded in the up dip mine over an area of about 400 m x 300 m. Rainfall infiltrating into the spoil in this up dip area becomes acid in the unsaturated zone, migrates downward and down dip in the spoil to the ponded zone, and then slowly leaks out through the crop barrier and a barrier between the mines to emerge as a major group of seeps.

This saturated zone appears to satisfy the requirements for *in-situ* sulfate reduction if organic material is introduced. The thick zone of ponded groundwater should lead to a thick anoxic layer overlain by a thin aerobic layer just beneath the water table in which dissolved O_2 is consumed by aerobic bacteria. Flow through the ponded zone is slow, estimated at .4 m/day giving time for sulfate reduction. Although the water table fluctuates by 1 to 2 m over the year, the ponded zone appears permanent, which is essential to prevent re-oxidation of FeS and regeneration of AMD.

The results from the laboratory experiments were used to implement a field test for *in-situ* sulfate reduction. Nearly 11.3 tons of sawdust mixed with 5 % by volume dolomite and 5 % by volume sewage sludge (to supply nutrients) were injected as a slurry with 13% solids into the saturated spoil at the Pot Ridge mine. A total of about 20 liters of an SRB culture was mixed into the slurry as it was injected. The slurry was injected through the drillstem into 4 drill holes spanning about 33 m (Figure 1). Previous efforts to complete drill holes using casing with coarse perforations were unsuccessful due to caving before the casing could be inserted. The slurry was mixed in a hydroseeder and pumped into the drill hole with a grouting machine or the hydroseeder pump at rates of about 300 L/min (75 gal/min). Little or no back pressure was encountered; the slurry seemed to flow into the hole essentially by gravity, indicating high porosity and large pores.

The sawdust was derived from a pile left from a sawmill near Portage, PA and was considerably degraded and mixed with soil (79.8% loss on ingnition, LOI) in comparison to fresh sawdust that was 99.7% LOI. Because of appreciable stone, bark and other coarse pieces, it was sieved to less than 1 inch to remove these materials.

The extent of spoil containing the sawdust slurry is not clear, but little sawdust could be noted in holes 10 m from the injection holes. If the spoil has 30% porosity, calculations indicate that 2.7% of the porosity is filled with sawdust.

Preliminary results after about 7 months indicate an inital rise in pH and alkalinity, and appreciable decrease in SO_4 in the injection area compared to an up dip well (Figure 1). Table 4 presents *in-situ* data for a monitoring well (MW-17) in the injection area and an up dip well (MW-20).

Table 4. Results for an *in-situ* injection well (MW-17) and an up dip monitoring well (MW-20). MW-17 was dry between days 51-107 due an extremely dry summer. Day 0 is July 26, 1995.

Injection well (MW-17)

Days	m		mS/cm	mg/L $CaCO_3$		mg/L						
	SWL	pH	Cond.	Acid.	Alk.	SO4	Fe	Mn	Al	Ca	Mg	TOC
37*	13.96	7.40	2560	0	686	1010	155	65	.1	352	154	251
51*	14.42	6.60	1090	0	407	1019	177	54	9.3	295	175	155
107*	13.87	5.66	1350	408	180	595	239	83	.8	191	147	83
145		4.60	1840	440	8.0	1534	86	90	17	171	197	2.1
189		3.30	2480	440	0	784	37	93	24	164	199	3.5
210**		3.70	1275	--	--	--	--	--	--	--	--	--

Up dip well (MW-20)

Days	m		mS/cm	mg/L $CaCO_3$		mg/L						
	SWL	pH	Cond.	Acid.	Alk.	SO4	Fe	Mn	Al	Ca	Mg	TOC
37*	18.50	3.90	6600	1540	0	4085	381	131	67	329	320	5.0
51*	18.93	4.00	6450	1660	0	3651	446	124	94	212	338	3.7
62		4.20	6690	1230	18	3088	404	132	84	258	337	4.9
76*	19.45	4.40	6500	1364	28	3082	477	128	91	261	338	6.4
90		5.00	5280	680	22	2400	247	114	14	306	252	3.2
107*	18.47	4.18	2950	1412	0	1275	467	126	100	236	202	NA
111		4.90	5960	962	18	3238	319	132	23	338	326	3.2
145		4.80	6370	1080	20	2946	284	126	13	363	323	3.0
189		3.20	7440	1940	0	1772	467	159	94	256	456	3.8
210**		4.60	3400	--	--	--	--	--	--	--	--	--

* Denotes PSU sampling dates. All other dates sampled by Mahaffey Labs, Grampian, PA.

** Monitoring is continuing and the samples from day 210 are being analyzed.

If the difference in SO_4 concentrations between the up dip well and the injection well was due to SO_4 reduction and the precipitation of FeS, then equal molar decreases in Fe would be expected. Redox potential was low enough (140 mV) within the injection area to support sulfate reduction, but persistent high concentrations of Fe suggest that sulfate reduction may not have been responsible for the large difference in SO_4 concentrations between MW-20 to MW-17. A decrease in TOC over time in MW-17 may suggest bacterial activity or dilution in the injection area. Increases in alkalinity and pH suggest that some acidity-consuming reactions are occurring. In addition to sulfate reduction the dissolution of dolomite is probably occurring. The possibility also exists that the organic matter in the sewage sludge adsorbed Fe, other metals and/or sulfur compounds. This could explain why the ratio of decreases in Fe to SO_4 are not concomitant.

A significant problem may be that MW-17 had only about 0.7 m of water at most sampling dates, whereas most sawdust was injected from 1 to 8 m deeper. Sulfate reduction may have been occurring beneath the completed portion of the well where anaerobic conditions are inferred to be prevalent. Figure 1 indicates that the geometry of the injection area may greatly influence the test results.

Another possible explanation for lack of clear evidence for SO_4 reduction is that deep water in MW-20 does not flow to the other monitoring wells. The water that is sampled from MW-20 may leak through sandstone units associated with the Brookville and Mercer coals and emerge as seeps to the northwest without mixing with overlying water. Because of this MW-20 samples may not reflect the up dip chemistry of the monitoring wells.

A third possibility is that there is little flow in the injection area, especially at MW-15 where the ponded area thins over the Brookville coal pit floor.

Discussion

Although the most rapid rate of sulfate reduction was obtained with whey (and lactate), this material has the disadvantage of being liquid, so it would presumable flow out of the spoil with the groundwater and would have to be replaced continuously. The possibility of organic outflow has been raised as a concern, though if appropriate concentrations were added the effluent concentration should be negligible. However, because of these potential problems, this option was not pursued, though it has potential. Discussions with milk processors indicate that whey is difficult to dispose of, and considerable quantities might be obtained.

Addition of alkalinity can stimulate the initiation of sulfate reduction. However, leaching from the alkaline material may initially increase concentrations in the effluent. For example, some fly ash and mushroom compost contains readily soluble $CaSO_4$. Over time the leaching will slow and eventually concentrations will decrease to less than or equal to influent concentrations. Initial alkalinity and increased pH in both the lab and field experiments is most likely the result of carbonate dissolution. Subsequent alkalinity generation is mostly the result of sulfate reduction.

Clearly, fresh sawdust did not support sulfate reduction as well as the degraded sawdust. This was also evidenced by Tuttle et al. (1969b) where partially degraded wood dust yielded more consistent sulfate reduction rates over a longer period of time than fresh sawdust in flask experiments. Here, the degraded sawdust with fly ash provided enough carbon to reduce not only all of the generated SO_4 from the fly ash, but also some of the influent SO_4 as well. This observation suggests that the degree of degradation of sawdust can affect sulfate reduction rates. Sulfate reduction using fresh sawdust may be limited by lignin, which protects plant cells from degradation. Also, the degraded sawdust may have been significantly broken down by fermentation of cellulose into simpler organics that SRB can use, but not so degraded that all of the reactive carbon is gone. Newspaper, mushroom compost and lactate all support sulfate reduction at similar rates.

Based on the average rate of SO_4 reduction obtained in the lab experiments, the reduction of sufficient SO_4 to create alkalinity adequate to neutralize the very high acidity of 1500 mg/L $CaCO_3$ found at the Pot Ridge mine would require a contact time of 500 days assuming 30% spoil porosity, 2.7% of porosity filled with sawdust and 2 moles of alkalinity for each SO_4 reduced. This very long contact time is not practical at the Pot Ridge site. However, several possible means of improving this performance can be suggested. Injection of higher sawdust concentrations, to perhaps 10% of the porosity, should proportionately increase the reduction effect. Also, the possibility of using milk processing wastes, which react more rapidly, exists.

An important question remaining is whether cellulose-type substrates will continue to degrade and react at rates similar to those measured. Eger and Wagner (1995) found that sulfate reduction markedly decreased in the third year of experiments with compost and sawdust and ceased in the fourth year, despite considerable carbon still available. Middelburg (1989) summarizes research on sulfate reduction in marine sediments indicating that the rate of organic carbon decomposition in recently deposited marine sediments decreases with time according to the equation:

$$\log k = -0.95 \log t - 0.81 \qquad (7)$$

where k is the rate of carbon decomposition by sulfate reduction (yr^{-1}), and t is time (yr). If this relation applies, then the rate of organic-sulfate reaction is predicted to decrease by a factor of about 9 between year 1 and year 10. To the extent that the organic matter in marine sediments is land-derived (which some undoubtedly is), then this rate of decrease might apply to the AMD system. This first order relationship follows the multi-G model which asserts that organic matter consists of many groups of compounds with different degradation rates (Westrich and Berner, 1984; Jorgensen, 1979). Marine organic matter tends to be more reactive than land plant wastes and the pH in the marine environment is higher than most AMD environments. Fe occurs as solid Fe-oxides rather than in solution in AMD, so the rate may decrease at a slower rate for the conditions applicable in this study. Tarutis and Unz (1994) showed similar trends for organic matter in wetlands exposed to AMD. Also, the rate of AMD generation probably drops off with time, so the required rate may be smaller.

Based on these data, the reaction rates we have derived should probably be considered a maximum rate, with a progressive decrease over a period of years. Probably only a field experiment over a long time period will be able to determine the long-term behavior of sawdust or similar materials exposed to AMD.

The sulfate reduction rates obtained in this study for cellulose and related materials are probably not the optimum that can be attained. The breakdown of the wood material by fermenting bacteria is probably the rate limiting step. Further experiments are needed to find fermenting bacteria that can accomplish this reaction more rapidly at acid pH values.

Conclusions

Bacterial sulfate reduction is capable of removing iron from AMD solutions and furnishing alkalinity to neutralize the acidity. Considerable sulfate is also removed. The process has no inherent maximum concentration that can be removed, in contrast to anoxic limestone drains. A variety of organic substrates can be used, including several forms of organic waste products such as milk processing wastes, sawdust, compost, and paper. If a sizable zone of anaerobic water-saturated spoil exists or can be created at a reclaimed surface mine, then AMD generated in the overlying unsaturated spoil can be partly or completely remediated within the spoil, thus obviating the need for surface treatment.

Experiments indicate that bacterial sulfate reduction can be initiated even at pH less than 3, though the rate is slow until about pH 5 is reached. Initial results from a field test show that slurries of organic particles can be injected into strip mine spoil in large quantities. Initially, there was a large rise in alkalinity and pH in the injection area, however these parameters have leveled off to pre-treatment values. It is possible that the monitoring wells are not deep enough to penetrate the anaerobic zone. Deeper wells are being drilled and sampled to ascertain the effects of sulfate reduction on AMD at depth in the spoil.

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