
Treatment of Acid Mine Drainage with Anaerobic Solid-Substrate Reactors

Author(s): William J. Drury

Reviewed work(s):

Source: *Water Environment Research*, Vol. 71, No. 6 (Sep. - Oct., 1999), pp. 1244-1250

Published by: [Water Environment Federation](#)

Stable URL: <http://www.jstor.org/stable/25045308>

Accessed: 14/02/2013 05:36

Your use of the JSTOR archive indicates your acceptance of the Terms & Conditions of Use, available at
<http://www.jstor.org/page/info/about/policies/terms.jsp>

JSTOR is a not-for-profit service that helps scholars, researchers, and students discover, use, and build upon a wide range of content in a trusted digital archive. We use information technology and tools to increase productivity and facilitate new forms of scholarship. For more information about JSTOR, please contact support@jstor.org.



Water Environment Federation is collaborating with JSTOR to digitize, preserve and extend access to *Water Environment Research*.

<http://www.jstor.org>

RESEARCH NOTE

Treatment of Acid Mine Drainage with Anaerobic Solid-Substrate Reactors

William J. Drury

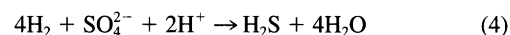
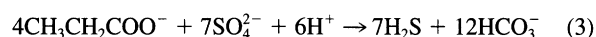
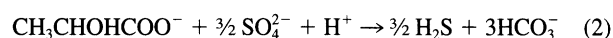
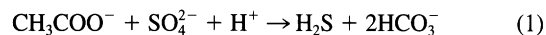
ABSTRACT: Anaerobic solid-substrate reactors were used in a laboratory study of acid mine drainage treatment. Parallel systems were run continuously for 23 months, both containing a solid substrate of 2:1 (weight) cow manure and sawdust. One system had cheese whey added with the mine drainage to provide an additional electron donor source to stimulate sulfate-reducing bacteria activity. Effluent pH from the reactor with whey addition was relatively constant at 6.5. Effluent pH from the reactor without whey addition dropped over time from 6.7 to approximately 5.5. Whey addition increased effluent alkalinity [550 to 700 mg/L as calcium carbonate (CaCO₃) versus 50 to 300 mg/L as CaCO₃] and sulfate removal (98 to 80% versus 60 to 40%). Sulfate removal rate with whey addition decreased over time from 250 to 120 mmol/m³·d, whereas it decreased from 250 to 40 mmol/m³·d without whey addition. Whey addition increased removal of dissolved iron (84 versus <0%), dissolved manganese (40 versus 2%), and dissolved zinc (99.7 versus 96.0%) in the second part of the experiment. Copper and cadmium removals were greater than 99%, and arsenic removal was 84% without whey addition and 89% with whey addition. Effluent sulfide concentrations were approximately 1 order of magnitude greater with whey addition. A 63-day period of excessive loading permanently decreased treatment efficiency without whey addition. *Water Environ. Res.*, 71, 1244 (1999).

KEYWORDS: acid mine drainage treatment, passive treatment, constructed wetlands, treatment wetlands, sulfate reduction.

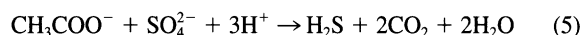
The use of anaerobic solid-substrate reactors for treating acid mine drainage (AMD) has been studied by a number of researchers (Dvorak, 1996; Dvorak et al., 1992; Eger, 1992; McIntire et al., 1990; Spotts et al., 1993; and Wildeman et al., 1993). In these systems, AMD is passed through a reactor filled with biodegradable solid waste such as manure, compost, or wood chips. Although numerous abiotic and microbially catalyzed reactions probably occur in these systems, it is hypothesized that sulfate reduction, mediated by sulfate-reducing bacteria (SRB), is primarily responsible for the pH neutralization and sulfate and toxic metals removal observed in these systems (Machemer and Wildeman, 1992, and McIntire et al., 1990).

Sulfate-reducing bacteria use a number of volatile fatty acids and hydrogen (H₂) as electron donors (Widdel, 1988). Sulfate-reducing bacteria activity consumes approximately one to two moles of protons (H⁺) per mole of sulfate (SO₄²⁻) reduced and produces approximately two equivalents of alkalinity per mole of

sulfate reduced. Exact number of protons consumed and alkalinity produced vary with the electron donor (acetate [CH₃COO⁻], reaction 1; lactate [CH₃CHOHCOO⁻], reaction 2; propionate [CH₃CH₂COO⁻], reaction 3; and H₂, reaction 4):

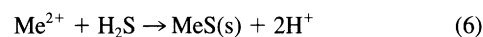


Reactions 1 through 4 portray neutralization of two to three equivalents of acidity per mole of sulfate reduced. Reactions 1 through 3 are written for pH ranging from 6.3 to 7.0. For lower pH values, carbon dioxide is produced instead of bicarbonate (HCO₃⁻). For such a pH, reaction 1 would be rewritten as

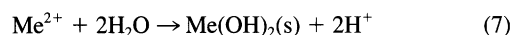


Although bicarbonate alkalinity is not produced in reaction 5, three moles of protons are consumed per mole of sulfate, which is reduced. Therefore, three acidity equivalents are neutralized in reaction 5 as they were in reaction 1. Similar exercises may be performed for reactions 2 and 3. The result is that SRB activity neutralizes two to three acidity equivalents per mole of sulfate reduced for the pH range of 7.0 to the lowest pH at which SRB will remain active (approximately 5.5 [Postgate, 1979]).

One mole of sulfide is generated per mole of sulfate reduction. Biogenically produced sulfide should precipitate metals that have a low metal-sulfide solubility product (reaction 6):



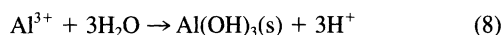
where Me²⁺ symbolizes a divalent metal with a low metal-sulfide solubility product. Alternatively, divalent metals may precipitate as metal hydroxides as the solution pH is neutralized (reaction 7)



The two protons released by reaction 6 or 7 would be neutralized by the alkalinity produced in reactions 1 through 3 or consumed in reactions 1 through 4. Because SRB activity reduces sulfate concentrations and produces alkalinity and sulfide, a decrease in

sulfate and aqueous-phase metals with low metal-sulfide solubility products and a pH increase should be evident if SRB activity has a significant effect on AMD treatment.

The rate at which AMD may be added to an anaerobic solid-substrate reactor without overwhelming its treatment capacity is a critical design consideration. The reactor loading rate described below assumes that the reactor will treat AMD properly as long as acidity of the AMD is neutralized. Loading rate, measured as a sulfate removal rate (SRR), can be developed in the following manner (Eger, 1992). Divalent cations that precipitate as metal sulfides or metal hydroxides release two moles of H^+ per mole of metal precipitated (reactions 6 and 7). Aluminum (Al) precipitation as a metal hydroxide also creates acidity, releasing (at most) three moles of H^+ per mole of Al (reaction 8)



Ferric iron (Fe^{3+}) will be reduced to ferrous iron (Fe^{2+}) in such reducing systems. It is probable that the electron donor for this reaction is organic matter, with the reaction catalyzed by iron-reducing bacteria. Different electron donors produce different amounts of acidity when oxidized by Fe^{3+} . Ratios are approximately 1:1 and vary from eight moles Fe^{3+} to seven equivalents of acidity when acetate is the electron donor to one mole Fe^{3+} to one equivalent of acidity with carbohydrate as the electron donor. If Fe^{2+} then precipitates as a sulfide or a hydroxide, approximately three moles of H^+ are released per mole of Fe^{3+} that is reduced. The large hydrogen ion concentration must be neutralized as well. The alkalinity generation required of SRB activity to produce a neutral pH is the sum of pH neutralization, $Al(OH)_3(s)$ precipitation, Fe^{3+} reduction, and divalent metal sulfide or hydroxide precipitation

$$SRR = \{0.5(1000 \times 10^{-pH}) + 1.5 \sum (\text{mmol/L of } Al^{3+} \text{ and } Fe^{3+}) \sum (\text{mmoles of metal sulfides formed, neglecting } Fe^{3+})\}Q \quad (9)$$

where SRR is the required sulfate reduction in mmol/time and Q is the flow rate through the reactor in L/time. Equation 9 assumes that all Al is Al^{3+} , one mole of Fe^{3+} reduction produces one equivalent of acidity, and two equivalents of alkalinity are formed per mole of sulfate reduced. The 1:1 relationship between sulfide production and metal-sulfide precipitation is not meant to replace traditional equilibrium chemistry as a description of metal-sulfide precipitation and is only relevant to the required sulfate reduction rate calculation.

Two solid-substrate reactors were run in parallel in this experiment. One system had only AMD run through a reactor filled with cow manure and sawdust. The second reactor, also filled with these solids, had cheese whey continually added to the reactor along with AMD. Adit water from the Crystal Mine, located 10 km (6 miles) north of Basin, Montana, was used as the model water in this examination of AMD treatment. Data were collected to evaluate the importance of sulfate reduction in, and develop design criteria for, anaerobic AMD biological treatment systems.

Materials and Methods

Water Source. Water draining from the adit of the Crystal Mine was collected on an as-needed basis (approximately bimonthly) and transported to the laboratory. Water was stored in covered plastic 19-L (5-gal) pails at room temperature. It was transferred to

Nalgene carboys and stored under a nitrogen head in a refrigerator at 4 to 9 °C when it was to be pumped to the reactors.

Water collected in June 1995 had low pH and high sulfate and metals concentrations compared to concentrations in other water collected. During the period that this highly contaminated water was used (day 335 to day 403), the reactors were stressed in maintaining an environment conducive for microbial growth by the high-strength AMD.

Reactor System. Two reactors were run in parallel. One reactor was run with whey supplementation and the other was run without whey supplementation. Both reactors were 660-mm-high polyethylene barrels. Acid mine drainage was pumped with a peristaltic pump into the bottom of the barrels, where 50-mm layers of 13-mm ceramic packing saddles that had been washed in 1.0 N hydrochloric acid (HCl) were located. Above this layer in each barrel were 45.4 L of a 2:1 (dry weight) mixture of cow manure and sawdust. The cow manure, from grass- and hay-fed cattle, and the sawdust, from lodgepole pine and Douglas fir, were each screened through 6-mm wire mesh to remove coarse particles before being mixed together. Substrate was compacted in 150-mm lifts at a pressure of $2.8 \times 10^{-3} \text{ kg/mm}^2$ (Spotts et al., 1993), producing a bulk dry density of 0.21 g/cm^3 . Monofilament nylon mats separated substrate from the lower packing layer and a 50-mm-thick packing layer above the substrate. Effective porosity of the substrate was measured by filling the reactors with water, allowing them to sit overnight, then allowing them to drain by gravity. Water volume drained from substrate divided by substrate volume produced an effective porosity of 23%. Aqueous samples were obtained from reactor effluents.

At the start of the experiment, both reactors were filled with Postgate's medium B (Postgate, 1979) and run in a batch mode for 2 weeks to grow a large population of SRB that would produce enough sulfide and alkalinity to withstand the shock of addition of AMD. After the batch-growth period ($t = 14$ days), Crystal Mine AMD was pumped to the reactors continuously. The flow rate to each reactor was set at 1.5 mL/min following the calculation procedure of Eger (1992). This calculation was performed using preliminary water quality data and an anticipated sulfate reduction rate of $300 \text{ mmol/d} \cdot \text{m}^3$ of substrate. On day 70, after it was clear that this sulfate removal rate would not be attained, flow rates were reduced to 0.9 mL/min to ensure that reactors were not being overloaded. Hydraulic retention times based on the effective porosity were calculated to be 4.8 days at 1.5 mL/min and 8.0 days at 0.9 mL/min. Reactor temperatures were not controlled and ranged from 14 to 24 °C.

Whey Source. A liquid carbon and energy source is typically not added continuously to solid-substrate reactors treating AMD (Wildeman et al., 1993). In this experiment, however, whey was used to stimulate SRB activity in one of the two reactors. It was collected from a cheese factory in Gallatin Gateway, Montana, and kept under refrigeration. Whey was added to one reactor at a ratio of 30 parts mine water to one part whey, by volume. Whey contains fermentable water-soluble proteins, lactose, and lactic acid (Hargrove and Alford, 1974, and Scott, 1981). Fermentation products and lactic acid supply SRB with a suitable carbon and energy source (McInerney and Beaty, 1988, and Widdel, 1988).

Analytical Techniques. Both pH and alkalinity samples were analyzed immediately after collection. A pH meter and combination pH electrode was used to measure pH, after a two-point calibration. The pH measurements made before day 200 were discarded because of quality assurance considerations. Alkalinity

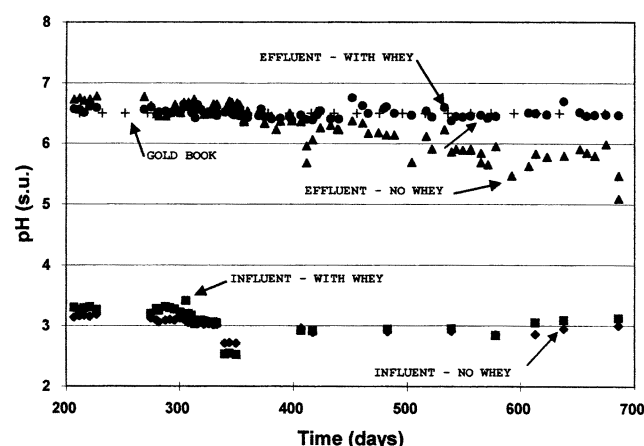


Figure 1—Mine drainage pH versus time for both reactors.

was measured according to *Standard Methods* (APHA et al., 1992) to an endpoint of 4.5, as measured on the pH meter. Alkalinity was not measured before day 306.

Sulfate samples were refrigerated until analysis. Sulfate was quantified on a Dionex Model 10 ion chromatograph (Dionex Corporation, Sunnyvale, California) for the first 11 months and a Dionex System DX500 ion chromatograph thereafter (Method 300, Pfaff et al., 1991). Metal samples were filtered through 0.45- μ m filters and acidified with concentrated HCl to a pH less than 2 before storage under refrigeration. Only dissolved (filtered) metals were analyzed. Early in the experiment, metals were quantified on a Perkin-Elmer (Norwalk, Connecticut) 5000 inductively coupled plasma (ICP) spectrometer using Method 6010A (U.S. EPA, 1986b). After day 400, a Perkin-Elmer Optima 3000 XL ICP spectrometer was used. Arsenic (As) could not be quantified on the Perkin-Elmer 5000 ICP; so As data is reported only for the period after day 400.

A limited number of sulfide analyses were performed in the fourteenth month of the experiment. Sulfide samples were analyzed immediately after collection. Sulfide was determined according to *Standard Methods* (APHA et al., 1992).

Statistical Methods. The effect of whey addition and of the high loading period from day 335 to day 403 was analyzed. Effluent pH, alkalinity, zinc (Zn), Fe, and manganese (Mn) from the two reactors were averaged for the periods from day 68 to day 334 and, including As, from day 404 to the end of the experiment. Data before day 68 were not statistically analyzed because reactors were in an artifactual startup period then. Data from day 335 to 403 were not used because the highly contaminated influent used during that period made the results atypical. Sulfate removal (influent concentration minus effluent concentration) was used instead of sulfate concentration to see whether whey addition affected sulfate removal, a key indicator of SRB activity. Copper (Cu) and cadmium (Cd) data were not analyzed statistically because many data were below the limits of detection.

For analysis of the effect of whey addition, an average of differences comparison was made at the 0.5 level using Student's *t* distribution (Berthouex and Brown, 1994). Differences in effluent concentrations from the two reactors or differences in sulfate removal were compared for days 68 to 334 and after day 403.

A white-noise, time-series approach was used to observe the

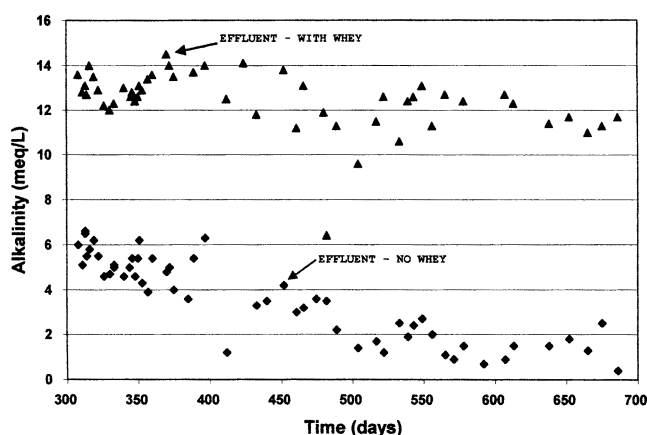


Figure 2—Alkalinity versus time for both reactors.

effect of addition of the highly contaminated water to the reactors at the 0.5 level with comparison to the periods before and after by a differences of two averages technique (Berthouex and Brown, 1994) using Student's *t* distribution on effluent concentrations. The before period was defined as day 68 to 334 and the after period was defined as day 404 to the end of the experiment.

Results

U.S. EPA "Gold Book" (U.S. EPA, 1986a) water-quality standards for chronic exposure are shown in the appropriate figures. This is to simplify comparison of the effluent data to criteria that may be an appropriate standard. For metals with standards that are functions of water hardness, standards at 100 mg/L calcium carbonate of hardness are shown.

The pH of the Crystal Mine AMD increased as it passed through the reactors (Figure 1). The bulk of neutralization occurred by the time water reached port 2 in both systems (data not shown). Effluent and port 2 samples from the whey-supplemented reactor contained more alkalinity than effluent and port 2 samples from the reactor without whey supplementation (Figure 2). Roughly one-half of the gain in alkalinity occurred before port 2 in both systems (data not shown).

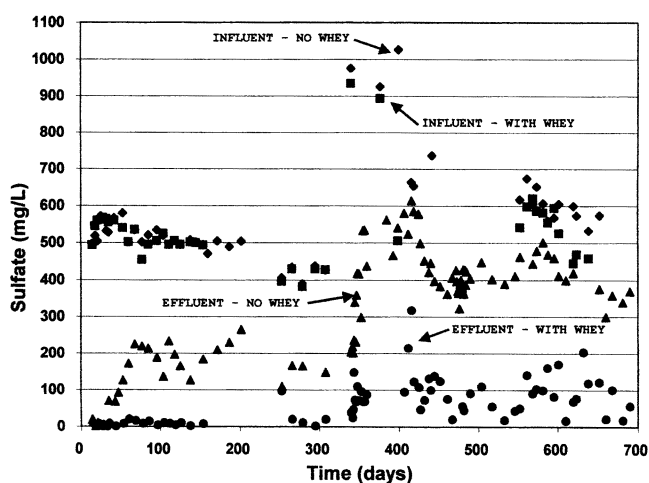


Figure 3—Sulfate concentrations versus time for both reactors.

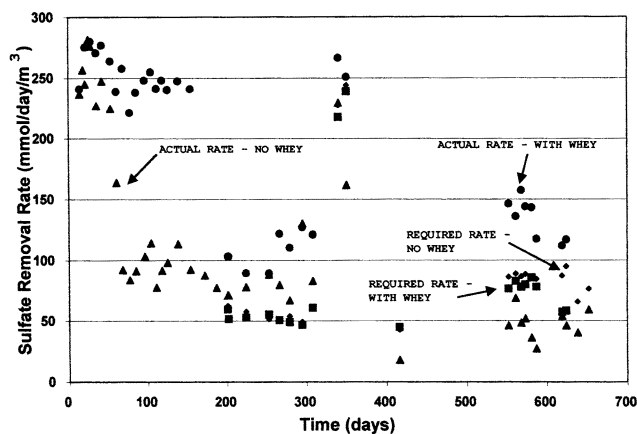


Figure 4—Sulfate removal rate versus time for both reactors.

Sulfate removal was significant in both reactors before day 335 with greater removal in the reactor with whey addition (Figure 3). The actual SRR decreased from 250 to 40 mmol/d·m³ substrate in the reactor without whey addition (Figure 4). With whey addition, the sulfate removal rate decreased from 250 to 120 mmol/m³·d substrate. Actual SRR was calculated by equation 10:

$$SRR_{\text{actual}} = (\text{SO}_4^{2-}{}_{\text{in}} - \text{SO}_4^{2-}{}_{\text{out}})Q/V \quad (10)$$

Where

SRR_{actual} = sulfate removed from water flow, mmol/m³·d substrate;

$\text{SO}_4^{2-}{}_{\text{in}}$, $\text{SO}_4^{2-}{}_{\text{out}}$ = influent and effluent sulfate concentrations, respectively, mmol/L; and
 V = volume of solid substrate, m³.

Actual SRR was compared to required SRR. Required SRR was calculated with equation 9, assuming that Fe, Zn, Cu, and Cd were precipitated as metal sulfides or metal hydroxides and that all Fe was Fe³⁺. Manganese was not included in this calculation because much of the Mn removal seemed to be from exchange adsorption. Aluminum, with an influent concentration averaging 12 mg/L, was included in calculations of the required SRR.

Zinc removal was 99.7% without whey addition and 99.8% with

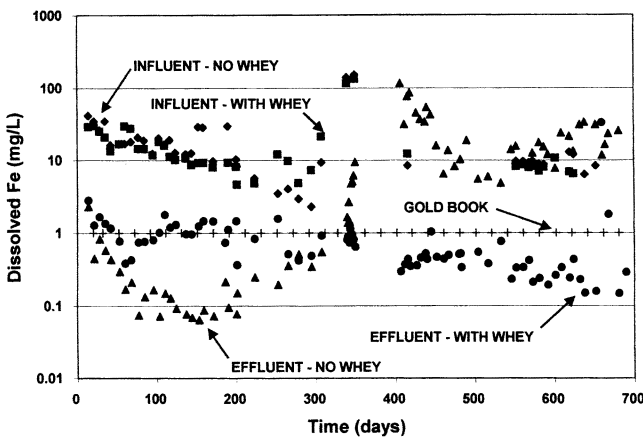


Figure 6—Iron removal versus time for both reactors.

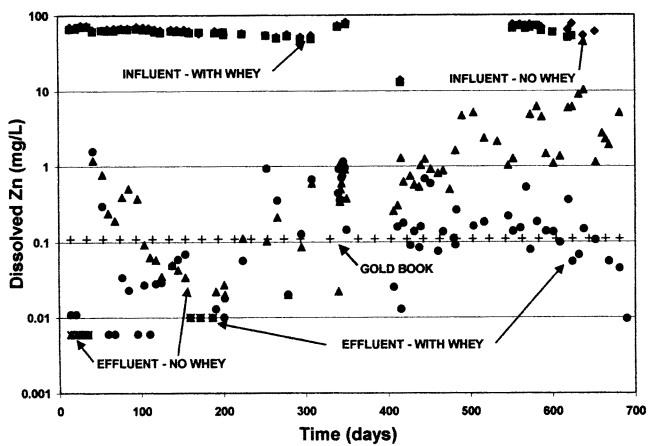


Figure 5—Zinc removal versus time for both reactors. Data below the detection limit are shown at the detection limit. These data are indicated with an asterisk (*) for the reactor without whey addition and with a circle (○) for the reactor with whey addition.

whey addition before day 335 (Figure 5). After day 403, Zn removal dropped to 96.0% without whey addition, whereas Zn removal with whey addition averaged 99.7%. Dissolved Fe was not removed from the water after day 403 without whey addition (Figure 6) but was removed (84.2%) with whey addition. Manganese removal without whey addition after day 403 was only 1.9% (Figure 7), but with whey addition removal was 39.6%. Copper (Figure 8) and Cd (Figure 9) were removed in excess of 99%. Arsenic removal was 84% in the reactor without whey addition and 89% in the reactor with whey addition (Figure 10). Effluent sulfide averaged 1.6 mg/L from the reactor without whey addition and averaged 12 mg/L from the reactor with whey addition.

Results of statistical analyses on the effect of whey addition are listed in Table 1. Whey addition had a positive effect on AMD treatment after the period during which the highly contaminated water was used. The highly contaminated water permanently decreased treatment efficiency without whey addition but did not affect treatment for sulfate removal, Zn removal, or Fe removal with whey addition.

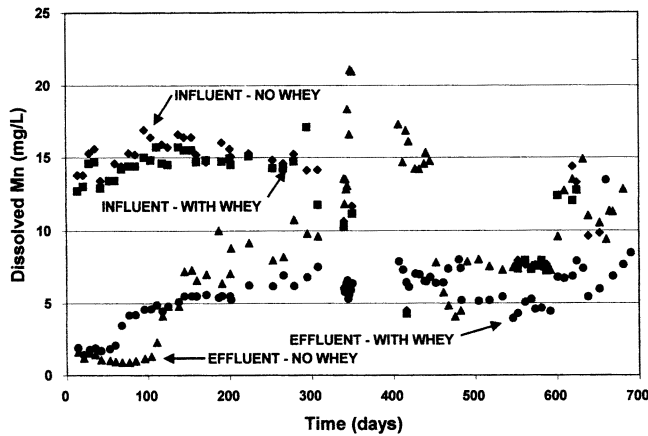


Figure 7—Manganese removal versus time for both reactors.

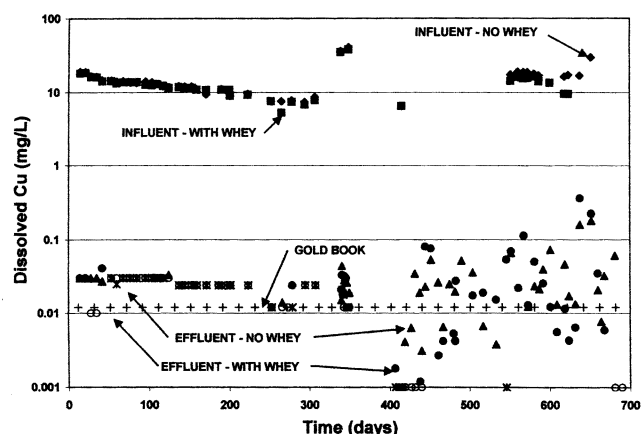


Figure 8—Copper removal versus time for both reactors. Data below the detection limit are shown at the detection limit. These data are indicated with an asterisk (*) for the reactor without whey addition and with a circle (○) for the reactor with whey addition.

Discussion

One experimental objective was to observe whether whey addition affects aqueous chemistry by neutralizing pH, reducing sulfate to sulfide, and precipitating metals through the effect of these two processes. Whey addition had a positive effect on sulfate removal after the period during which the highly contaminated water was pumped through the reactors (Table 1). Sulfate removal is the most common method of assessing SRB activity (Postgate, 1979, and Smith, 1993). Whey addition also improved pH neutralization. Therefore, the pH increase in these reactors is likely to be influenced by SRB activity (Machemer and Wildeman, 1992, and McIntire et al., 1990).

The whey-supplemented reactor produced higher alkalinity than the reactor without whey addition (Table 1), which is consistent with increased sulfate reduction. Organic acids from the whey may have been present and would have neutralized acidity in the pH

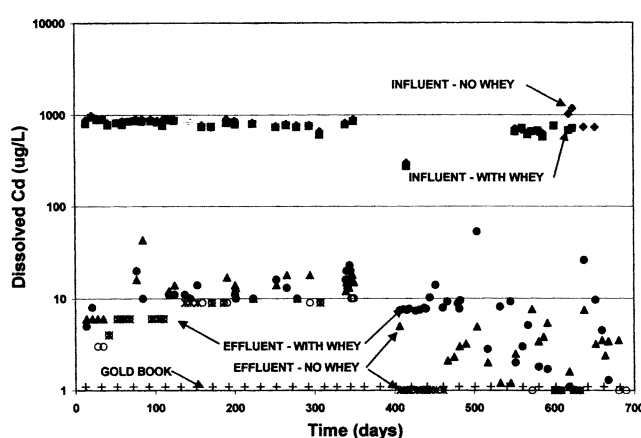


Figure 9—Cadmium removal versus time for both reactors. Data below the detection limit are shown at the detection limit. These data are indicated with an asterisk (*) for the reactor without whey addition and with a circle (○) for the reactor with whey addition.

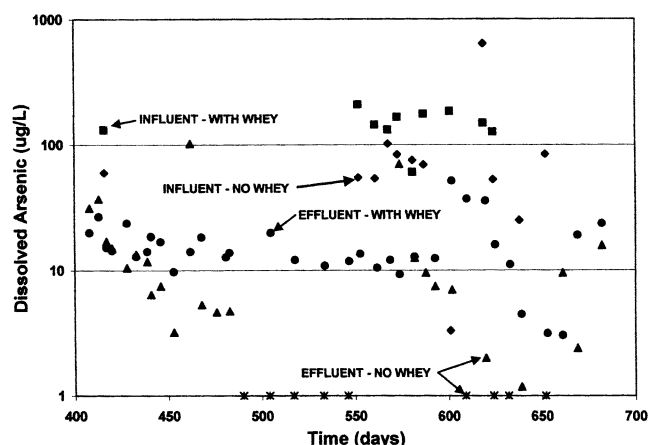


Figure 10—Arsenic removal versus time for both reactors. Data below the detection limit are shown at the detection limit. These data are indicated with an asterisk (*) for the reactor without whey addition and with a circle (○) for the reactor with whey addition.

range covered by the alkalinity titrations. Ammoniafication of whey proteins would also have produced alkalinity.

Whey addition had a significant, positive effect on sulfate removal (Table 1). Effluent sulfate concentrations increased after day 403 in the reactor without whey addition but were relatively constant in the reactor with whey addition (Figure 3). Sulfate-reducing bacteria could mediate sulfate reduction to a greater degree when whey was added because more organic molecules serving as carbon and energy sources were available for SRB to catalyze reactions 1 through 3. Because SRB cannot use insoluble organic matter as their carbon and energy source (Widdel, 1988), the SRB could be carbon limited in an organic medium containing cow manure and sawdust. These materials are mostly polymers of cellulose and hemicellulose (Dinwoodie, 1989; Hobson et al., 1981; and Stafford et al., 1980), which cannot be directly used by SRB. Sulfate should not have been limiting SRB activity in the reactor without whey addition because sulfate concentrations were more than 1 order of magnitude greater than published half-saturation coefficients for sulfate-limited systems (Okabe, 1992; Smith, 1993; and Urban et al., 1994).

Whey addition had a positive effect on Zn, Mn, and Fe removal after day 403 (Table 1). Greater pH and sulfide concentrations with whey addition increased metal hydroxide and metal sulfide precipitation. Manganese was probably removed primarily by exchange adsorption before day 335, until breakthrough occurred in the reactor without whey addition. Effluent data (Figure 8) show exchange-adsorption breakthrough curves. High effluent Mn concentrations during the addition of highly contaminated water immediately after day 335 are further evidence for exchange adsorption. Manganese previously adsorbed to the substrate could have been exchanged by cations such as Fe, Zn, Cd, and Cu, which are more strongly bound to solid organic matter (Kerndorff and Schnitzer, 1980; Stumm and Morgan, 1996; and Turner et al., 1981). The reactor with whey addition did not have as high effluent and port 2 Mn concentrations after day 340, indicating that Mn may have been retained by a mechanism other than exchange adsorption, possibly sulfide or hydroxide precipitation.

The greater Fe removal in the reactor with whey addition

Table 1—Statistical analysis of the effects of whey addition and the effect of addition of highly contaminated water.

Parameter	With vs. without whey		Before vs. after addition of highly contaminated water	
	Before high load	After high load	No whey reactor	Whey reactor
Sulfate removal	With better ^a	With better	Before better	No difference
pH	Without better	With better	Before better	Before better
Alkalinity	With better	With better	Before better	Before better
Zinc	No difference	With better	Before better	No difference
Iron	Without better	With better	Before better	No difference
Manganese	No difference	With better	Before better	Before better
Arsenic	—	No difference	—	—

^a Better means that effluent concentrations were statistically lower at the $\alpha = 0.05$ level for metals, statistically higher at the $\alpha = 0.05$ level for pH or alkalinity, and statistically larger at the $\alpha = 0.05$ level for sulfate removal.

indicates that sulfide or hydroxide precipitation contributed to the enhanced treatment. As with Mn, Fe concentrations in the reactor without whey addition exhibited breakthrough curves indicative of exchange adsorption (Figure 6) and breakthrough behavior is not evident from the reactor with whey addition.

The high loading period (day 335 to day 403) permanently decreased effluent Zn, Fe, and Mn concentrations from the reactor without whey addition (Table 1). Copper and Cd concentrations were probably not affected because enough sulfate was reduced in each reactor to precipitate these metals, which have quite low metal sulfide and metal hydroxide solubility products. In the reactor with whey addition, apparently enough sulfate was reduced to precipitate Zn and Fe during and after high loading conditions.

The highly contaminated water used between days 335 and 403 overloaded the reactor without whey addition in terms of its ability to maintain effective water treatment and an environment conducive for SRB activity (Table 1). Acceptable loading occurs when the acid neutralized by SRB activity equals or exceeds the acidity load caused by the pH of the influent water and the protons liberated from metal precipitation and Fe^{3+} reduction (as shown in equation 9). That the reactor without whey addition never recovered from the overload conditions is evident in Figures 4, 5, and 6, where the Zn and Fe concentrations were higher when actual SRR was less than required SRR. Effluent pH was closer to neutral when actual SRR exceeded required SRR (Figure 11).

Reactor loading rate is used by designers as a sizing criterion for anaerobic biological reactors treating AMD (Eger, 1992, and Wildeman et al., 1993). Given a flow rate and water chemistry, and with a forecasted SRR, a reactor volume is calculated with equation 9. Although required SRR can be expected to be relatively constant over time, in this experiment actual SRR without whey addition decreased with time (Figure 4). The solid substrate probably initially contains some readily biodegradable organic compounds, which spurs high initial SRRs. After the readily biodegradable matter is depleted only less readily biodegradable matter remains to be used by bacteria (Middelburg, 1989). These compounds are degraded at a slower rate, which reduces the SRR. This sequence would cause the observed decreasing SRR. Designers of reactors without continuous addition of a carbon and energy source should account for a decrease in the SRR when only short-term data are available. Replenishment of the carbon and energy source in reactors without continuous addition of such material will

eventually be necessary in reactors designed for significantly high SRRs.

Conclusions

Whey addition improved long-term treatment efficiency for pH neutralization, alkalinity production, and sulfate, Fe, Zn, and Mn removal. Overloading the reactor without whey addition for 63 days permanently decreased treatment efficiency for pH neutralization and sulfate, Fe, Zn, and Mn removal. Water treatment was effective if the SRR was greater than that required by influent water chemistry. The SRR in the reactor without whey addition decreased from 250 to 40 mmol/m³·d substrate; with whey addition, the sulfate removal rate decreased from 250 to 120 mmol/m³·d of substrate. After day 403, Zn removal was 96.0% without whey addition and 99.7% with whey addition. Iron removal was almost nil without whey addition and 84% with whey addition. Manganese removal was 2% without whey addition and 40% with whey addition. Copper and cadmium were removed in excess of 99%. Arsenic removal was 84% without whey addition and 89% with whey addition.

Acknowledgments

Credits. This work was initially supported by the U.S Environmental Protection Agency through the Department of Energy and

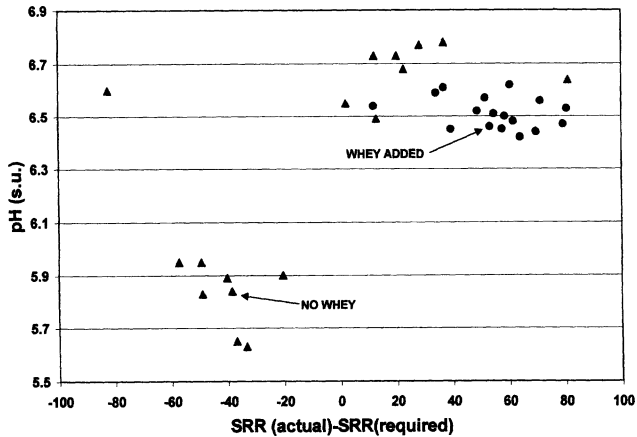


Figure 11—Effluent pH versus the sufficiency of the sulfate reduction rate.

Contract Number DE-AC22-88ID12735. Atlantic Richfield Corporation (ARCO), Anaconda, Montana, supported the second year of the project. The author thanks John Pantano of ARCO for his support of the project. The late William Chatham of the Department of Chemistry and Geochemistry at Montana Tech provided many of the chemical analyses. Crystal Mine water was collected by Chatham, Fred Kratz, and Wayne Olmstead. Students who assisted on the project were Fred Kratz, who constructed the reactors and had a significant role in the experimental design, Jason Brabec, and William Ballinger.

Author. William J. Drury is an associate professor in the Environmental Engineering Department at the Montana Tech of the University of Montana. Correspondence should be addressed to William J. Drury, Environmental Engineering Department, Montana Tech, 1300 West Park Street, Butte, MT 59701-8997.

Submitted for publication August 5, 1997; revised manuscript submitted August 8, 1998; accepted for publication March 8, 1999.

The deadline to submit Discussions of this paper is January 15, 2000.

References

- American Public Health Association; American Water Works Association; and Water Environment Federation (1992) *Standard Methods for the Examination of Water and Wastewater*. 18th Ed., Washington, D.C.
- Berthouex, P.M., and Brown, L.C. (1994) *Statistics for Environmental Engineers*. Lewis Publishers, Boca Raton, Fla.
- Dinwoodie, J.M. (1989) *Wood: Nature's Cellular, Polymeric Fibre-Composite*. The Institute of Metals, London and Brookfield, Vt.
- Dvorak, D.H. (1996) The Feasibility of Using Anaerobic Water Treatment at the Hardin Run Clay Mine. Rep. to Crescent Brick Company, New Cumberland, W.Va. U.S. Bureau Mines, Pittsburgh, Pa.
- Dvorak, D.H.; Hedin, R.S.; Edenborn, H.M.; and McIntire, P.E. (1992) Treatment of Metal-Contaminated Water Using Bacterial Sulfate Reduction: Results from Pilot-Scale Reactors. *Biotechnol. Bioeng.*, **40**, 609.
- Eger, P. (1992) The Use of Sulfate Reduction To Remove Metals from Acid Mine Drainage. *Am. Soc. Surf. Min. Reclamation Meeting*, Duluth, Minn.
- Hargrove, R.E., and Alford, J.A. (1974) Composition of Milk Products. In *Fundamentals of Dairy Chemistry*. B.H. Webb, A.H. Johnson, and J.A. Alford (Eds.), Avi Publishing Company, Westport, Conn.
- Hobson, P.N.; Bousfield, S.; and Summers, R. (1981) *Methane Production from Agricultural and Domestic Wastes*. Applied Science, London.
- Kerndorff, H., and Schnitzer, M. (1980). Sorption of Metals on Humic Acid. *Geochim. Cosmochim. Acta* (G.B.), **44**, 1701.
- Machemer, S.D., and Wildeman, T.R. (1992) Adsorption Compared with Sulfide Precipitation as Metal Removal Processes from Acid Mine Drainage in a Constructed Wetland. *J. Contaminant Hydrol.*, **9**, 115.
- McInerney, M.J., and Beaty, P.S. (1988) Anaerobic Community Structure from a Nonequilibrium Thermodynamic Perspective. *Can. J. Microbiol.*, **34**, 487.
- McIntire, P.E.; Edenborn, H.M.; and Hammack, R.W. (1990) Incorporation of Bacterial Sulfate Reduction into Constructed Wetlands for the Treatment of Acid and Metal Mine Drainage. *Proc. 1990 Natl. Symp. Min.*, Univ. Ky., Lexington, 207.
- Middelburg, J.J. (1989) A Simple Rate Model for Organic Matter Decomposition in Marine Sediments. *Geochim. Cosmochim. Acta* (G.B.), **53**, 1577.
- Okabe, S. (1992) Rate and Stoichiometry of Sulfate Reducing Bacteria in Suspended and Biofilm Cultures. Ph.D. thesis, Mon. State Univ., Bozeman.
- Pfaff, J.D.; Brockhoff, C.A.; and O'Dell, J.W. (1991) The Determination of Inorganic Anions in Water by Ion Chromatography—Method 300.0. U.S. EPA, Environ. Monit. Syst. Lab., Cincinnati, Ohio.
- Postgate, J.R. (1979) *The Sulphate-Reducing Bacteria*. Cambridge Univ. Press, Cambridge, G.B.
- Scott, R. (1981) *Cheesemaking Practice*. Applied Science, London.
- Smith, D.W. (1993) Ecological Actions of Sulfate-Reducing Bacteria. In *The Sulfate-Reducing Bacteria: Contemporary Perspectives*. J.M. Odom and R. Singleton, Jr. (Eds.) Springer-Verlag, New York.
- Spotts, E.; Mitchell, T.S.; Hoschouer, C.T.; and Schafer, W.M. (1993) Evaluation of Organic Substrates for Use in Wetlands Constructed To Treat Acid Mine Drainage. *Proc. Sixth Billings Symp. Plann., Rehabilitation, Treat. Disturbed Lands*, Billings, Mont., 170.
- Stafford, D.A.; Hawkes, D.L.; and Horton, R. (1980) *Methane Production from Waste Organic Matter*. CRC Press, Boca Raton, Fla.
- Stumm, W., and Morgan, J. (1996) *Aquatic Chemistry*. 3rd Ed., Wiley & Sons, New York.
- Turner, D.R.; Whitfield, M.; and Dickson, A.G. (1981) The Equilibrium Speciation of Dissolved Components in Freshwater and Seawater at 25°C and 1 atm Pressure. *Geochim. Cosmochim. Acta* (G.B.), **45**, 855.
- Urban, N.R.; Brezonik, P.L.; Baker, L.A.; and Sherman, L.A. (1994) Sulfate Reduction and Diffusion in Sediments of Little Rock Lake, Wisconsin. *Limnol. Oceanog.*, **39**, 797.
- U.S. Environmental Protection Agency (1986a) *Quality Criteria for Water*. EPA-440/5-86-001, Off. Water Regul. Stand., Washington, D.C.
- U.S. Environmental Protection Agency (1986b) *Test Methods for Evaluating Solid Waste—Physical/Chemical Methods*. SW-846, 3rd Ed., Off. Solid Waste Emergency Response, Washington, D.C.
- Widdel, F. (1988) Microbiology and Ecology of Sulfate- and Sulfur-Reducing Bacteria. In *Biology of Anaerobic Microorganisms*. A.J.B. Zehnder (Ed.), Wiley Interscience, New York, 469.
- Wildeman, T.; Brodie, G.; and Gusek, J. (1993) *Wetland Design for Mining Operations*. BiTech Publishers, Ltd., Richmond, B.C., Can.