

## **MODELING OF SULFATE REDUCTION IN ANAEROBIC SOLID SUBSTRATE BIOREACTORS FOR MINE DRAINAGE TREATMENT**

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### **ABSTRACT**

A mathematical model is presented for the rate of sulfate reduction in anaerobic solid substrate bioreactors and subsurface flow wetlands used to treat water containing heavy metals. In these systems, sulfate is reduced to sulfide through bacterial sulfate reduction (BSR). The sulfide precipitates metals with low metal sulfide solubility products, and BSR produces alkalinity. It is assumed that neither the bioreactors nor the wetlands receive significant replenishment of electron donor (organic carbon), and that they operate solely on the organic carbon included in the substrate during system construction. The model predicts sulfate reduction as a function of the initial age of the organic matter, hydraulic retention time, and temperature. The hydraulic retention time must be long if system reconstruction, supplying more organic carbon, is to be done infrequently. It takes about seven years for a substrate with a high initial age (2 years) to achieve a larger sulfate reduction rate than a substrate with a low initial age (0.5 years). The required hydraulic retention time for 50 percent sulfate reduction varies from 8 d at 17°C to 41 d at 1°C. *KEY WORDS:* acid mine drainage treatment, passive treatment, constructed wetlands, treatment wetlands, sulfate reduction.

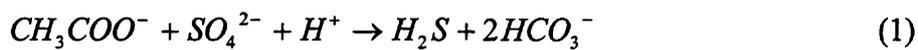
### **BACKGROUND**

There are over 25,000 inactive mine sites and exploration prospects in the western United States, and drainage from these sites has caused significant water quality problems (USGS, 1999). In Montana alone, there are over 8,000 abandoned or inactive hard rock mines and milling sites (Hargrave and Metesh, 1999). Potentially responsible parties for the abandoned mines often cannot be located or, if located, have insufficient funds to pay for water treatment. Also, many abandoned mines are difficult to access in winter because they are at high elevation where snowfall is severe. The nearest electrical power lines may be miles away. If power lines were to be installed to these abandoned mine sites, they would likely experience frequent failures because of the high snowfall and strong winds produced by winter storms. Seasonal (good

weather) treatment is not an option, since failure to treat acid mine drainage (AMD) for a short period in any season can harm the ecology of the receiving stream for years.

Treatment systems for abandoned mine sites must therefore be inexpensive to build and operate. The systems must be reliable and effective enough to meet surface water quality standards. Anaerobic solid substrate bioreactors and subsurface flow wetlands have been constructed for treating AMD at abandoned mine sites (Machemer *et al.*, 1990; Kepler and McCleary, 1994; Eger and Wagner, 1995; Dietz and Stidinger, 1996; Dvorak, 1996; Sobelowski, 1996; Mueller *et al.*, 1997) and in the laboratory (Bolis *et al.*, 1991; Dvorak *et al.*, 1992; Whiting *et al.*, 1994; Sikora *et al.*, 1996; Manyin *et al.*, 1997). In these systems, AMD passes through a reactor or wetland filled with biodegradable solid waste such as manure, compost, or wood chips. An advantage of such systems is that neither electrical power nor the frequent attention of an operator are required.

While numerous abiotic and microbially-catalyzed reactions occur in these systems, sulfate reduction, mediated by sulfate-reducing bacteria (SRB) (Brock and Madigan, 1991; Widdel, 1988), is primarily responsible for pH neutralization and sulfate and toxic metals removal (Machemer and Wildeman, 1992; McIntire *et al.*, 1990). Bacterial sulfate reduction (BSR) produces approximately two moles of alkalinity per mole of sulfate that is reduced; the exact amount of alkalinity varies with the structure of the electron donor. An example reaction with acetate as the electron donor shows this alkalinity production ratio (Reaction 1):



One mole of sulfide is generated per mole of sulfate reduction, and the sulfide will precipitate heavy metals with low metal sulfide solubility products (Reaction 2):



where  $Me^{2+}$  symbolizes a divalent heavy metal.

A design process for solid substrate bioreactors and SSF wetlands has been described (Eger, 1992; Wildeman *et al.*, 1993). The acidity load to the system is calculated by summing the free hydrogen ions in the influent plus hydrogen ions that would be released through metal precipitation (for example, Reaction 2). Since one mole of sulfate reduction typically produces two moles of alkalinity (Reaction 1), the system is sized by dividing the acidity load by one half of the anticipated sulfate reduction rate in moles/day/m<sup>3</sup>. A major problem is forecasting what the sulfate reduction rate will be, since it depends on the biodegradability of the organic substrate and the temperature. Additionally, the hydraulic retention time affects the amount of sulfate reduction, because more electrons from solid substrate degradation will be transferred to the

water if the retention time is long. This paper describes a mathematical model that takes into account the effect of substrate degradability, temperature and hydraulic retention time.

## MODEL DEVELOPMENT

BSR depends on the presence of an electron donor at a low oxidation-reduction potential to deliver electrons to the sulfate. If the significant electron donors in solid substrate bioreactors and SSF wetlands are the solid organic matter built into the substrate during construction, BSR will decrease over time as the electron donors get depleted.

One model for prediction of electrons released per year, in carbon equivalents, by the degradation of solid organic matter ( $G$ ) is the declining  $k$  model (Middelburg, 1989):

$$\frac{dG}{dt} = -k_G(t)G(t) \quad (3)$$

The coefficient  $k_G$  will decrease over time because as time progresses, the remaining organic matter will be less biodegradable and will therefore decay more slowly than the organic matter that has already decayed. Microbes utilize easy to degrade organic matter initially and attack the harder to degrade matter after the more bioavailable matter is gone (Westrich and Berner, 1984; Middelburg, 1989). Some solid organic matter will be only partially degraded. An end product of their degradation is humus, a colloidal polymer that is quite recalcitrant (Bohn *et al.*, 1985; Benner *et al.*, 1988). The biodegradability of the original organic matter can be described by including an apparent initial age  $a$  in the expression of the time variability of the rate coefficient (Janssen, 1984; Middelburg, 1989):

$$k_G(t) = b(a + t)^m \quad (4)$$

$b$  and  $m$  are empirical coefficients in this model.

A second model for the degradation of solid organic matter is the multiple  $G$  pool model (Westrich and Berner, 1984). This model considers the solid organic matter to consist of a number of different organic compound types, or pools, which degrade at different rates. Each pool has its own degradation rate coefficient. However, detailed data is lacking on the number of significant pools and their rate coefficients for degradation. Westrich and Berner (1984) analyzed phytoplankton degradation into two pools and found that degradation of the easy-to-degrade pool was no longer significant after two months. The multiple  $G$  pool model was not used for modeling AMD treatment systems in this paper because analysis of the amount of matter in the different pools is difficult, as is measurement of the rate coefficients for each pool. Only one pool - the hard-to-degrade pool - appears to be significant in AMD treatment systems. Another

complication is attempting to measure the production of matter in one pool from the partial degradation of matter in another pool – humification.

The rate-limiting step in BSR in these systems is the solubilization rate of the solid organic matter by cellulolytic and hemicellulolytic bacteria (Eastman and Ferguson, 1981; Westrich and Berner, 1988; Barlaz *et al.*, 1989; Bechard *et al.*, 1994). SRB kinetics should be, in this case, zero order in sulfate concentration. However, experimental data indicates that the sulfate reduction rate is much higher near a reactor inlet than near the reactor outlet. In one experiment, the sulfate reduction rate in the first half of a cow manure- and sawdust-filled reactor was 2.5 times higher than the sulfate reduction rate in the second half of the reactor. Sedimentation of the substrate may have influenced this result, but sedimentation would have decreased the pore volume in the first half of the reactor and increased the pore volume in the second half, thus decreasing the hydraulic residence time in the first half and increasing it in the second half. The relative importance of these competing phenomena has yet to be determined. To account for the decrease in sulfate reduction over reactor length, a first order relationship ( $k_s S$ ) for sulfate degradation was placed into the model.

Some conversion factors must be added to the model to mathematically convert the rate of organic matter degradation into BSR. One such factor ( $\eta$ ) converts the number of electrons released by organic carbon degradation to those electrons actually used in BSR.  $\eta$  has not been determined for anaerobic solid substrate bioreactors or SSF wetlands. Studies of sulfate-containing marine sediments report  $\eta$  to be in the range of 0.5 to 1.0 (Urban *et al.*, 1994). The same paper reported  $\eta$  to be 0.78 in a sulfate-enriched freshwater sediment. Martens and Klump (1984) measured it to be 0.68 in marine sediments. It is expected that in bioreactors and SSF wetlands that  $\eta$  would be relatively high, since these continuous-flow systems continually bathe the degrading particles in sulfate-rich water. A second factor ( $\beta$ ) is the ratio of solid volume to water volume in the substrate:

$$\beta = \frac{1 - e}{e} \quad (5)$$

where  $e$  is the substrate porosity.  $\beta$  accounts for the relatively high BSR rate that will occur in a system with a large amount of organic matter per unit of water. A third factor ( $f$ ) converts the mass of organic carbon degrading per unit time to the mass of sulfate that is reduced. Using an ideal plug flow reactor model to describe advective transport, the mathematical model for BSR is:

$$\frac{dS}{d\tau} = -f\beta\eta\left(-\frac{dG}{dt}\right)k_s S \quad (6)$$

where  $\tau$  is the hydraulic residence time. Integrating (6) for an influent sulfate concentration of  $S_0$ , and an effluent concentration of  $S$  at a residence time of  $\tau$  yields:

$$S = S_0 \exp(-f\beta\eta k_G(t)G(t)k_s\tau) \quad (7)$$

where  $k_s$  is the rate coefficient for sulfate removal, and  $\tau$  is the hydraulic retention time in days.

### MODEL PARAMETERS

$G(t)$  was calculated as a function of time ( $t$ ) using an integrated form of Equations (3) and (4):

$$G(t) = G(0) \left( \frac{a+t}{a} \right)^{(-b)} \quad (8)$$

$G(0)$ , the amount of solid organic matter initially present in a bioreactor or SSF wetland, was estimated in the following manner. The average volatile solids content measured in a substrate of two parts cow manure to one part sawdust (dry weight) was 48%. The dry density was measured to be  $0.21 \text{ g cm}^{-3}$ . Assuming that all volatile solids were organic matter with an average formula of  $\text{CH}_2\text{O}$  (40% carbon),  $G(0)$  was  $0.084 \text{ g carbon per cm}^3$  for this substrate.  $k_G$  was calculated using Equation 4 with  $b = 0.16$  and  $m = -1$  (Middelburg, 1989). After being calculated in this manner,  $k_G$  was divided by 365 days per year to make its units correspond with the hydraulic residence time being measured in days.

$\beta$  was measured to be 3.3 on the cow manure and sawdust substrate. An  $\eta$  of 0.75 was used in the calculations. Based on Reaction 1,  $f$  was set equal to 4 g  $\text{SO}_4$  per g organic carbon.  $k_s$  and  $a$  were determined from sulfate reduction data in a 23 month experiment (Drury, 1999). In this experiment, AMD was pumped through a reactor filled with the cow manure and sawdust substrate at a  $\tau$  of eight days. Sulfate was quantified in influent and effluent samples. The method of least squares was used to fit  $k_s$  and  $a$  to the sulfate concentrations.

Temperature will affect the BSR rate. The Arrhenius equation is commonly used for adjusting rate coefficients for temperature (Westrich and Berner, 1988):

$$k_T = A \exp(-E/RT) \quad (9)$$

where  $A$  is a pre-exponential factor,  $E$  is the activation energy,  $R$  is the ideal gas law constant, and  $T$  is absolute temperature. Westrich and Berner (1988) found the activation energy for a sulfate-reducing marine sediment system to be approximately 65 kJ/mol.  $k_s$  was calculated using data from a reactor operated at an average temperature of  $17^\circ\text{C}$ . Equation (8) was used to correct  $k_s$  for temperatures of  $1^\circ\text{C}$ ,  $5^\circ\text{C}$  and  $10^\circ\text{C}$ .

## MODEL RESULTS AND DISCUSSION

The  $k_S$  and  $a$  that fit the experimental data best were  $1.4 \text{ cm}^3 \text{ g SO}_4^{-1}$  and  $0.95 \text{ yr}$ , respectively. Over the range tested, the initial age  $a$  does not appear to be a sensitive parameter for modeling sulfate removal in these solid substrate bioreactors (Figure 1). These modeling results appear to agree with the conclusion of Tarutis and Unz (1994) that the substrate initial age becomes insignificant after about three years of operation. The need for designers to consider the decrease in sulfate removal over time is apparent.

Eventually, a substrate with a high initial age (well composted before system construction) should outperform substrates with lower initial ages. Younger substrates degrade quickly compared to older substrates, losing many of their electrons in a short time. However, the sulfate reduction rate for a substrate with an initial age of 2.0 years does not begin to equal that of a substrate with an initial age of 0.5 years until after seven years of operation according to the model. Since the model was constructed using data from a 23-month experiment, the result from such an extrapolation is to be used with caution.

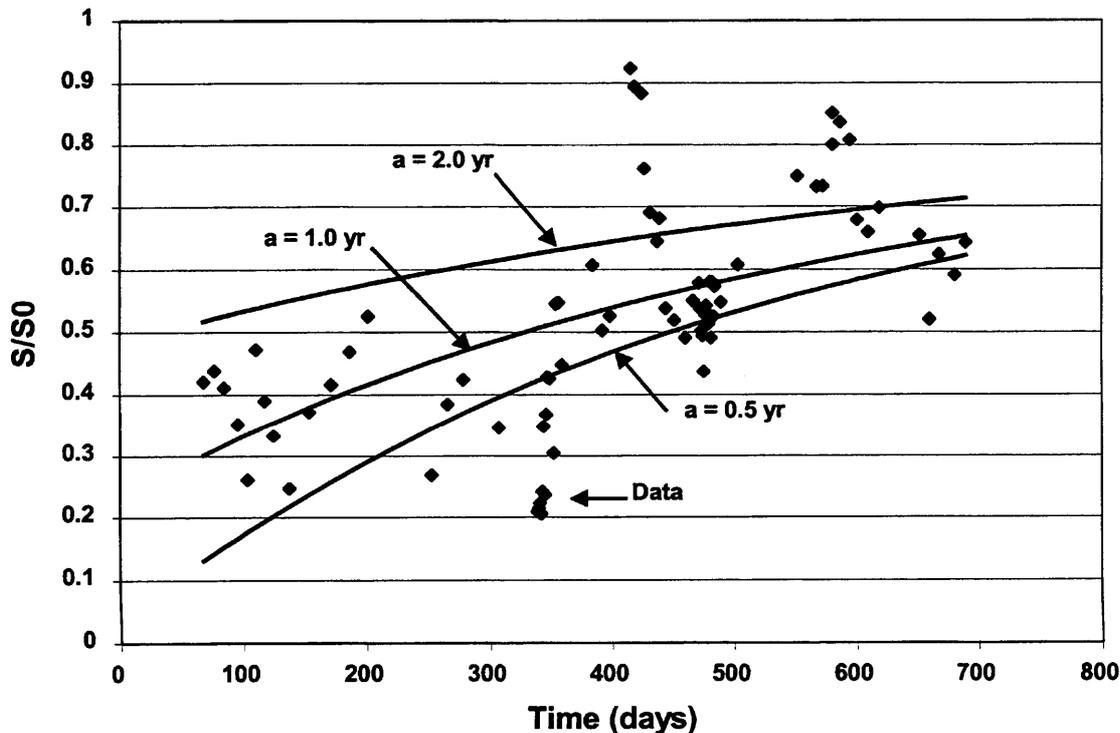


Figure 1. Modeled effect of initial age on sulfate reduction.  $S/S_0$  is the effluent sulfate concentration divided by the influent sulfate concentration.

In designing an anaerobic solid substrate bioreactor or SSF wetland, a minimum hydraulic

retention time must be specified. Use of a low hydraulic retention time corresponds to a commitment to frequently replenish the carbon and energy source for the bacteria (Figure 2). The longer the hydraulic retention time, the longer a solid substrate may be used before it is replaced. For example, if reduction of 50% of the influent sulfate is required for good water treatment, the  $\tau$  should be 14 days if the substrate is changed every two years, or it should be 25 days if the substrate is to be changed every four years.

Temperature has a significant effect on sulfate reduction, with systems at low temperatures requiring higher  $\tau$ 's to achieve the same sulfate reduction as systems at higher temperatures (Figure 3). For example, the required  $\tau$  for 50% sulfate reduction at 17°C is only 8 days, but is 41 days at 1°C. The critical temperature for system design is the winter temperature; systems should be designed to operate properly at that worst-case temperature.

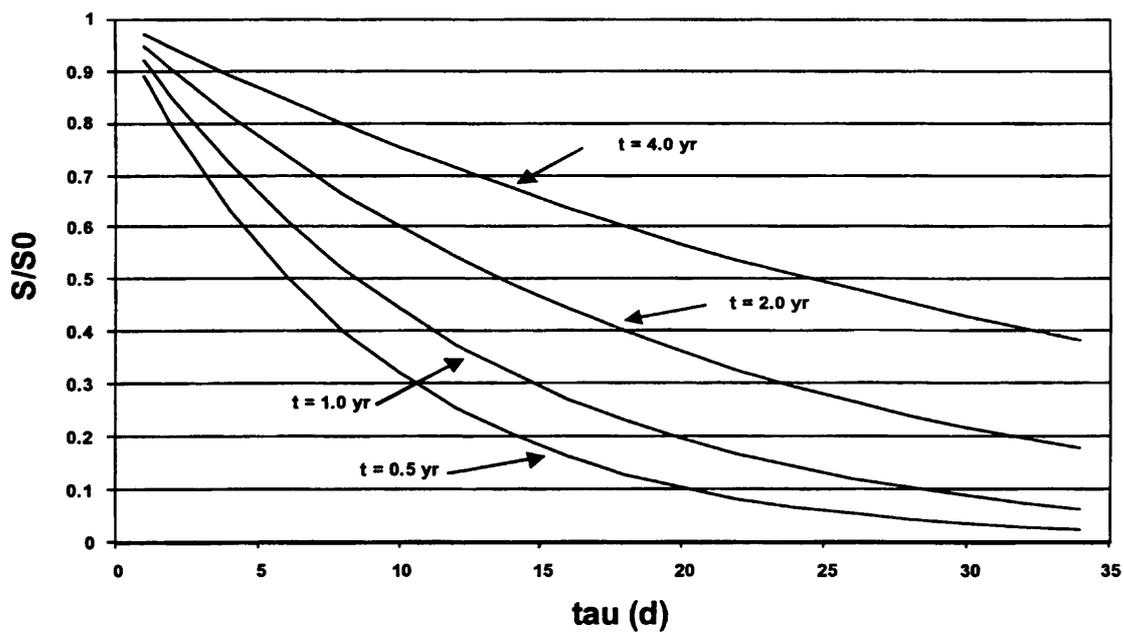


Figure 2. Modeled effect of hydraulic retention time ( $\tau$ ) on sulfate reduction.  $t$  is the substrate replacement interval.

### CONCLUSIONS

1. The minimum effective hydraulic retention time and the interval between substrate replacement are interrelated. The retention time must be long if substrate replacement, supplying more organic carbon, is to be done infrequently.

2. Substrates with low initial ages are more effective in reducing sulfate than substrates with high initial ages early in the life of the system. Sulfate reduction by a substrate with a high initial age will eventually exceed that from a substrate with a low initial age. According to the model, this will occur after about seven years of system operation for a substrate with a high initial age (2 years) compared to one with a low initial age (0.5 years).
3. Temperature significantly affects sulfate reduction. The required hydraulic retention time for 50 percent sulfate reduction varies from 8 d at 17°C to 41 d at 1°C according to the model.

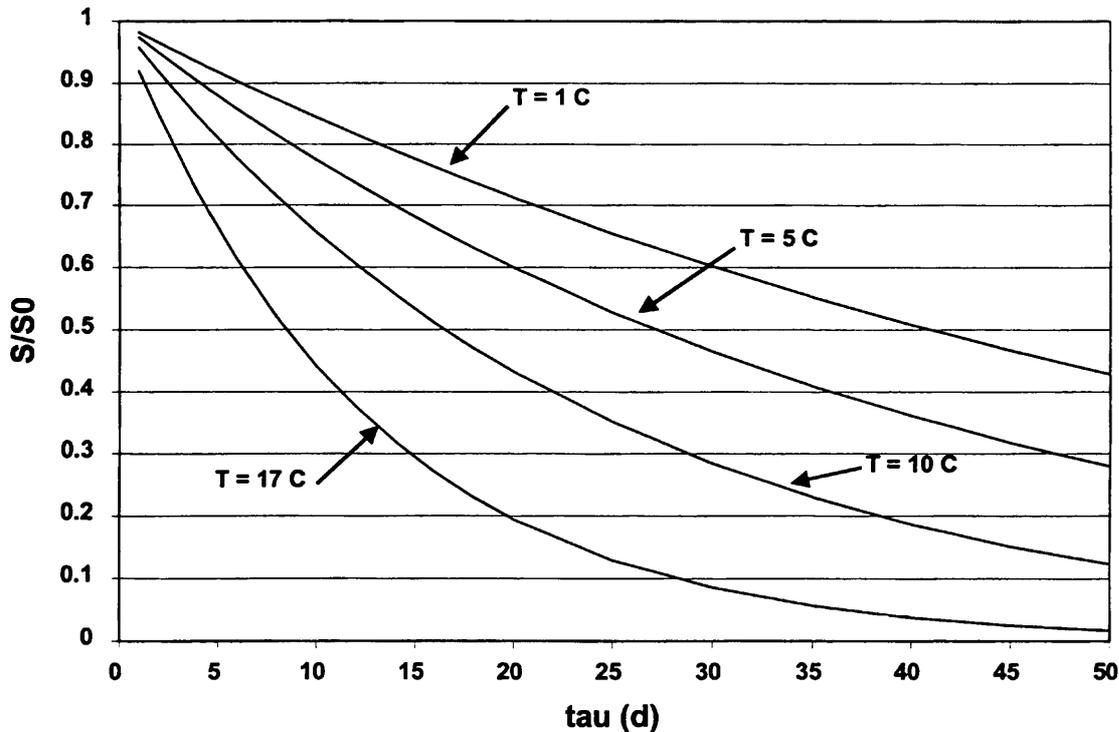


Figure 3. Modeled effect of temperature on sulfate reduction.

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