Effects of Armoring on Limestone Neutralization of AMD

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Abstract

The metal concentration of an acid solution has a significant effect on the neutralization rate of that solution. Dissolved iron in acid mine drainage not only coats limestone surfaces and hinders dissolution rates,but iron hydrolysis and precipitation reactions increase the required neutralization time. Our objective was to develop an empirical model for the neutralization rate of acid mine drainage by limestone. The effects of limestone surface area, dissolved iron concentration and iron armoring were modeled explicitly. The derived model, when refined and properly calibrated will allow for the improved design of open limestone channels.

Introduction

Limestone is an inexpensive and effective agent for the neutralization of waste acid streams low in dissolved iron and manganese. Although acid mine drainage (AMD) can contain appreciable concentrations of iron and manganese, limestone is the neutralizing agent of choice for AMD treatment. The magnitude, extent and longevity of AMD pollution, and the lack of a financially responsible party for many AMD discharges makes cost an overriding factor when considering treatment alternatives.

The amount of limestone needed for a passive AMD treatment system is typically determined by multiplying the annual acid load by the desired lifetime of the system. This 'mass-based' or equilibrium approach has two principal disadvantages. First, AMD neutralization systems are not at equilibrium, even at discharge. Second, dissolved iron and manganese form insoluble precipitates on the limestone surface (Loeppert and Hossner, 1984; Evangelou et al., 1992). This armoring process hinders limestone dissolution and compromises the effectiveness of the treatment system. Any rationally-based passive treatment design must account for both of these factors

Limestone Dissolution

The equilibrium reactions for limestone dissolution are fairly straightforward,

$$\mathrm{CaCO_3 + 2H^+ \leftrightarrow Ca^{2+} + H_2O + CO_2} \tag{1}$$

$$\mathrm{CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-} \tag{2}$$

and equilibrium constants are available for a wide range of temperatures and pressures. It is relatively easy to calculate the concentrations of products in systems open and closed to the atmosphere (Garrels and Christ, 1965). Limestone dissolution kinetics on the other hand is quite complicated,

$$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^- \tag{3}$$

$$CaCO_3 + H_2CO_3^* \leftrightarrow Ca^{2+} + 2HCO_3^- \tag{4}$$

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-} \tag{5}$$

These reactions occur in parallel, and involve a direct attack on the surface by protons (Eq. 3), the partial pressure of carbon dioxide (Eq. 4) and water (Eq. 5) (Stumm and Morgan,1996 and references therein).

Limestone dissolution rate constants are typically determined by either the pH-stat or the free-drift technique. When limestone is added to strong acid, the pH increases, the rate is determined primarily by the initial acid concentration. The amount of acid required to keep the pH constant (pH-stat) or the change in pH (free-drift) is directly related to the limestone dissolution rate. Mixing rate and particle size must be kept constant, and parameters such as temperature, partial pressure of carbon dioxide, etc., are systematically varied to determine their effect. Using these approaches, Plummer et al. (1978) determined that limestone dissolution rate (R) was a first order reaction and independent of the partial pressure of CO_2 in the pH range 3 to 5

$$R = k_1 a_{H^+} \tag{6}$$

where k_1 is the first order rate constant and a_{H^+} is the hydrogen ion activity. The overall rate equation has been given as,

$$R = k_1 a_{H^+} + k_2 a_{H_2CO_3^*} + k_3 a_{H_2O} - k_4 a_{Ca^{2+}} a_{HCO_3^-} \tag{7}$$

where all symbols have their usual interpretation (Plummer et al., 1978).

The reason particle size has to be controlled in limestone dissolution rate experiments is because of the well-known effect of surface area on dissolution rates (Figure 1). This relationship has been used to quantify different carbonate minerals in mixtures (Turner, 1960; Turner and Skinner, 1960; Evangelou et al., 1984) and to deduce particle size distributions of soil carbonates (von Tress et al., 1984; Moore et al., 1990). Despite the importance of surface area in limestone neutralization rates, surface area is not a factor in the design of passive acid mine drainage treatment systems. The reason for this is that there is no easy way to determine the surface area of coarse porous media like limestone rocks.

Surface Area

The two most common methods for determining the surface area of coarse particles are 1) coating particles with paint or metal powder and measuring the change in mass, and 2) the use of shape factors with the length of one or more particle axes. Gas desorption methods are not appropriate because of the low specific surface of coarse media. Garga et al. (1991) used a nickel coating-differential mass method to determine the surface area of crushed limestone. Based on a statistical

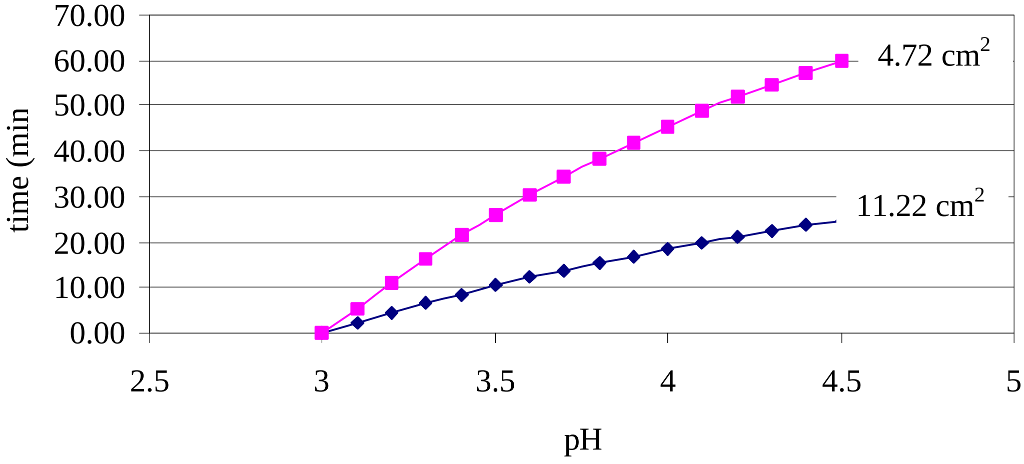

Figure 1. The neutralization rate of acid solutions containing two different-sized limestone particles. Decreasing the total surface area of limestone in contact with the solution increases the amount of time required to reach a given pH.

analysis of measurements of individual particles, they derived the relationship,

$$A_{MS} = \frac{3.89}{b^{1.08}} \tag{8}$$

where A_{MS} is the mass-specific surface area and b is the length of the intermediate orthogonal axis. Pearson and McDonnell (1977) used a painting technique to calibrate an empirical model based on a shape factor (S) and the maximum particle dimension (L, 'a' in Figure 2). The shape factor was calculated as,

$$S = 1.15 - 0.25\frac{L}{D} \tag{9}$$

where D is the equivalent spherical diameter, and the surface area (A) was calculated as,

$$A = \frac{4.84}{S}\left(\frac{W}{U}\right)^{2/3} \tag{10}$$

where W is particle mass and U is unit mass. Sabin and Hansen (1994) calculated the volume-specific surface area, A_{vs}, as

$$A_{vs}^{(\text{actual})} = r_e A_{vs}^{(\text{perfect ellipsoid})} \tag{11}$$

where r_e is the shape factor,

$$r_e = R_{\text{oblate}} R_{\text{rough}} \tag{12}$$

R_{oblate} is a measure of the deviation of an ellipsoid from a sphere, and R_{rough} is a measure of the deviation of an ellipsoidal rock from a perfect ellipsoid. All of these methods are effective, but they are rather tedious to perform.

Iron Armoring

Anoxic mine water can hold more dissolved Fe^{2+} than Fe^{3+}. When this anoxic water is exposed to the atmosphere, the Fe^{2+} oxidizes to Fe^{3+}, and the relatively insoluble Fe^{3+} hydrolyzes and precipitates from solution

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3\mathit{(s)} + 3H^+ \tag{13}$$

$$Fe^{3+} + H_2O \leftrightarrow Fe(OH)^{2+} + H^+ \tag{14}$$

$$Fe^{3+} + 2H_2O \leftrightarrow Fe(OH)_2^+ + 2H^+ \tag{15}$$

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3^0 + 3H^+ \tag{16}$$

$$Fe^{3+} + 4H_2O \leftrightarrow Fe(OH)_4^- + 4H^+ \tag{17}$$

This 'AMD sludge' or 'yellowboy' coats rocks and fills in the pore spaces in streambeds. For flow-through passive treatment systems like open limestone channels, these iron hydrolysis and precipitation reactions have two implications. First, by coating the limestone, there is less surface area available for limestone dissolution. Second, the iron precipitation reactions take time, that is, there is not an immediate increase in pH.

The mechanisms by which iron armors limestone is poorly understood, although it appears that Fe^{3+} does not physically bind to the limestone surface (Loeppert and Hossner, 1984). Armored limestone has been estimated to be from to 4-62% as effective as fresh limestone (Pearson and McDonnell, 1975; Ziemkiewicz et al., 1997). In an acid solution containing limestone and iron oxide, there are two sinks for protons: calcite dissolution (Eq. 1) and iron oxide dissolution (Eq. 13). Experimental procedures that do not account for iron in the neutralization reaction may overestimate armored limestone dissolution rates.

Because Fe^{3+} solubility decreases as pH increases (up to the zero point of charge), when an iron containing acid solution is neutralized, iron oxides must precipitate from solution (Figure 2). Because these precipitation reactions take time to occur (Dousma and de Bruyn, 1976), the presence of iron in a solution essentially introduces a lag in the neutralization process. This lag time must be accounted for in the neutralization reactions in open limestone channels.

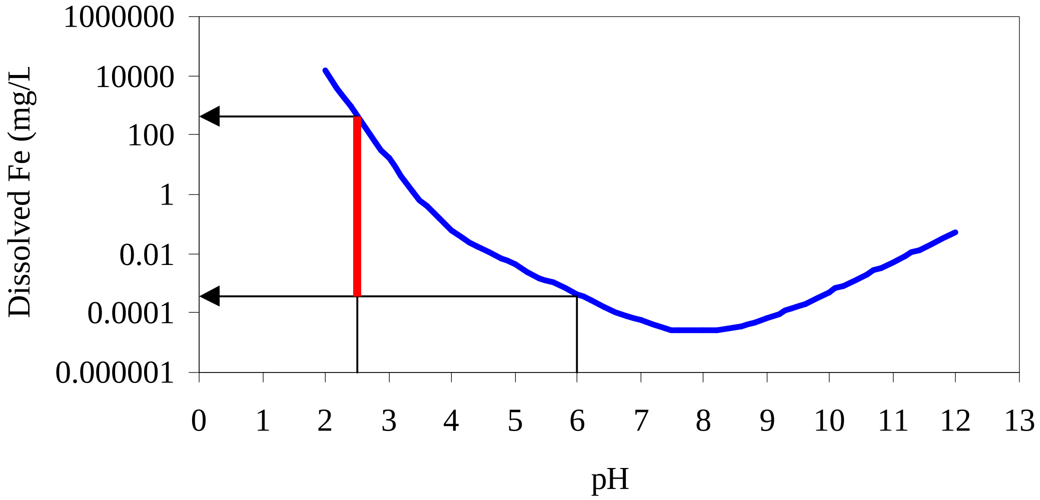

Figure 2. Overall dissolved iron solubility as a function of pH for a solution containing 500 ppm SO_4. Assuming an initial pH of 2.5 and a desired final pH of 6.0, the thick vertical line represents the mass of iron that must be removed by precipitation. Equilibrium constants from Lindsay (1979).

Ziemkiewicz et al., (1997) were the first to try to account for both the kinetic and armoring processes in the neutralization of acid mine drainage. They used the approach of Pearson and McDonnell (1977) to estimate surface area and a first-order limestone dissolution model. To account for the effects of armoring, Ziemkiewicz et al. (1997) assumed that armored limestone was 20% as effective as fresh limestone (Pearson and McDonnell (1975). In general, the first-order model under-predicted acid neutralization in the open limestone channels they investigated.

Our objective was to develop a model for the neutralization rate of acid mine drainage by limestone. Rather than develop an overall rate equation similar to Eq. 7, we chose to model the process empirically. The effects of limestone surface area, dissolved iron concentration and iron armoring were used as dependent variables.

Materials and Methods

All limestone came from Germany Valley, West Virginia, which has a $CaCO_3$ equivalent of about 98.5% (Zurbuch, 1996). Ellipsoidal limestone was collected from the Blackwater River Limestone Drum Station, sieved into five diameter classes and washed with dilute acid and deionized water. Crushed limestone was prepared in the same manner. An approach similar to Sabin and Hansen (1994) was used to estimate limestone surface area. Solutions containing 100 g limestone, with and without armoring, and 400 mL acid solution, with and without iron, were monitored continuously for pH (Accumet 25 pH meter and Accu-pHast Electode, Fisher Scientific, Pittsburgh, PA). At predetermined time intervals, a small (0.9 mL) aliquot of the solution was collected for calcium and iron analysis by inductively coupled plasma spectroscopy (Perkin-Elmer P4000) or atomic absorption spectroscopy (Perkin-Elmer 5000).

Results and Discussion

Figure 3 shows representative data for the effects of limestone surface area on the neutralization rate of proton-only acid solutions (no iron). As expected, increasing the limestone surface area (at constant limestone mass) increases the neutralization rate. Increasing the surface area by about six-times decreases the time required to reach pH 7 by about two and a half-times. Figure 4 shows representative data of the effect of dissolved iron on the neutralization of an acid solution by limestone. The lag time introduced by dissolved iron is evident, as is the increase in reaction time required to reach some final pH. Figure 5 shows the effect of coating thickness on the neutralization rate of a 0.100 mM Fe solution. Iron was added to the solution to eliminate iron oxide dissolution as a proton sink during the reaction (Eq. 13). Increasing the coating thickness decreased the neutralization rate of the solution.

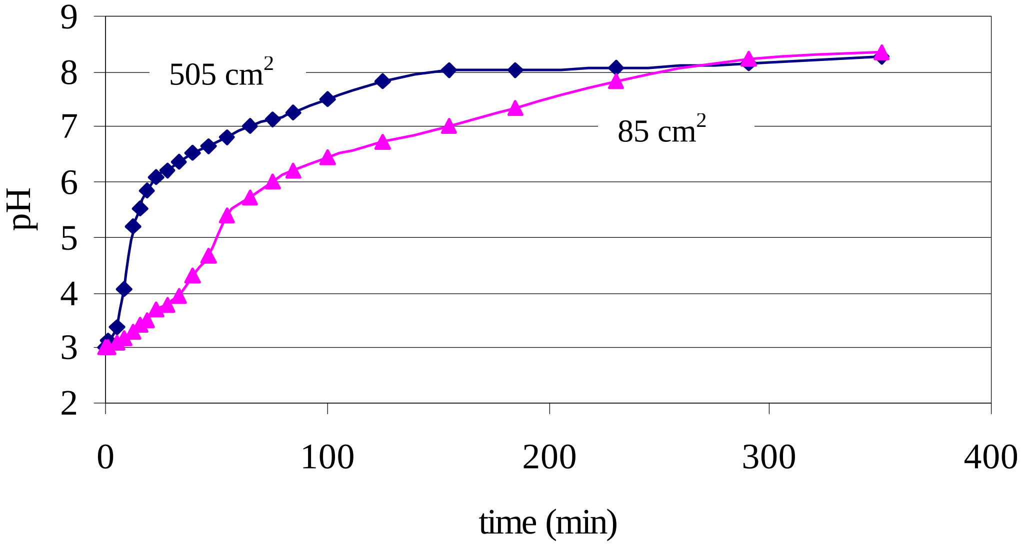

Figure 3. Effect of limestone surface area on the complete neutralization of an acid solution without iron. Both systems have the same mass of limestone, initial pH and final pH, but the rate at which they reach that final pH is faster for the system containing the larger limestone surface area. This figure differs from Figure 1 in that both systems have the same mass of limestone.

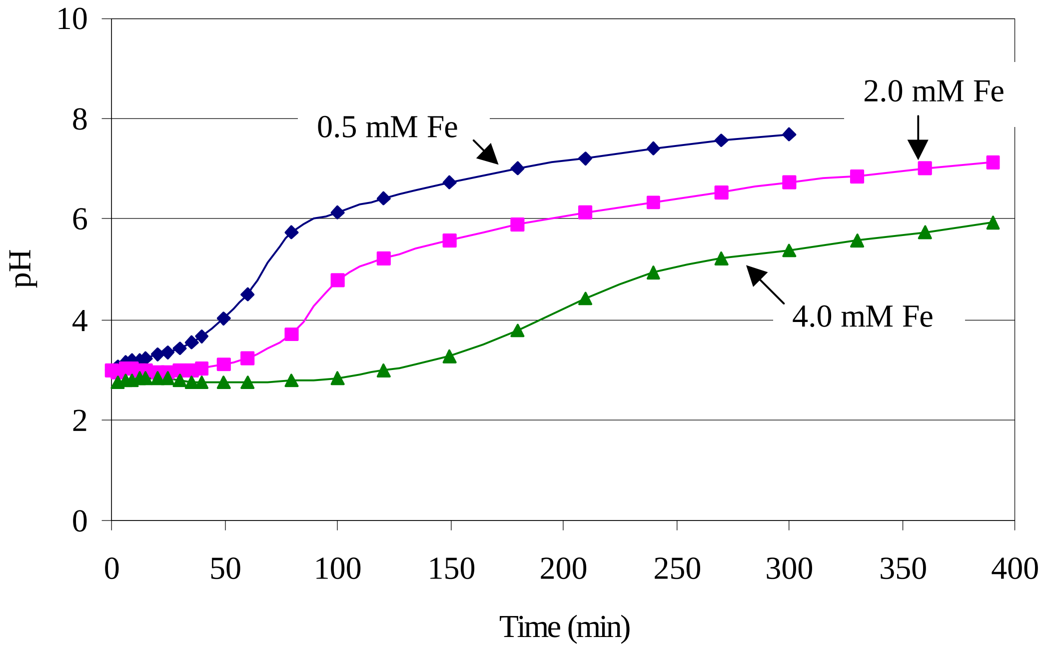

Figure 4. Effect of iron concentration on the neutralization rate of acid solutions by limestone. Increasing the iron concentration increases the lag time before neutralization begins and increases the total amount of time required to reach some final pH.

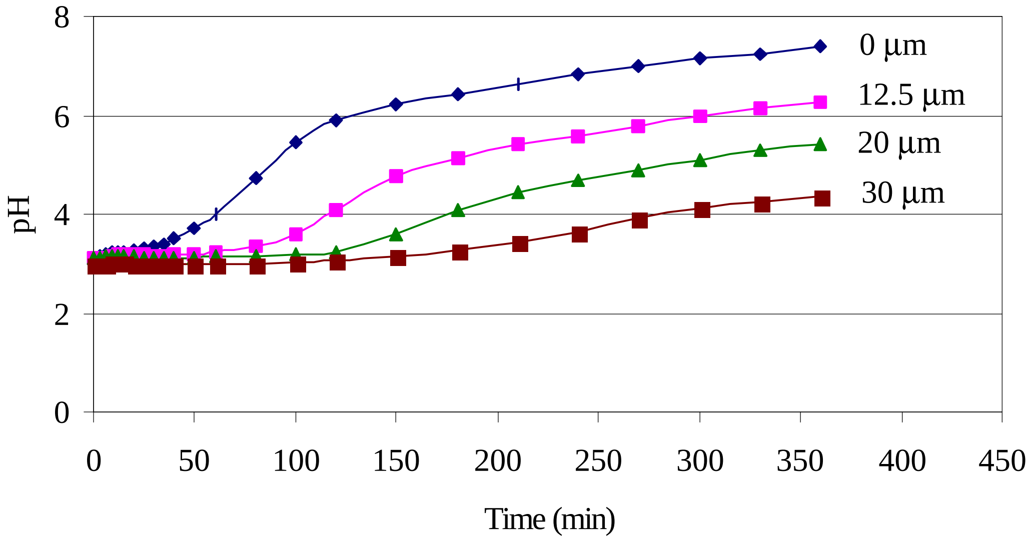

Figure 5. Effect of the thickness of the iron oxide coating on the neutralization of 0.100 mM Fe solution. Increasing the thickness of the armor decreases the neutralization rate and increase the time required to reach some final pH.

An empirical equation was fit to data similar to Figures 3 - 5 for a range in particle size (surface area), initial pH, initial Fe^{3+} concentration, final pH, and coating thickness,

$$
\begin{aligned}
t = e^{0.0654\,b}\Big[\left(-75.08\,pH_f + 338.27\right) + 0.8053\,pH_f^{3.5346}\Big]* \\
A_{MS}^{(-0.1305\,pH_f + 0.6185)\,pH_i + (0.7365\,pH_f - 4.5918)} + \\
\left(24.538\,pH_f^2 - 272.44\,pH_f + 765.29\right)[Fe]
\end{aligned}
\qquad (17)
$$

where, t is the required reaction time, b is the thickness of the iron oxide coating (μm), pH_f is the final pH, A_{MS} is the specific surface area of limestone (cm^2/g), pH_i is the initial pH, and [Fe] is the initial iron concentration (mM).

Because Eq. 17 is an empirical model, the coefficients have no physical meaning. It does however allow us to compare scenarios and make relative interpretations of the effect of various parameters on the resulting water quality. For example, consider a discharge with a flow of 1000L/min, an initial pH of 3.0 and 55 mg/L dissolved Fe. Using the mass-based approach and a desired lifetime of 10 years, we can use Eq. 17 to optimize the limestone particle size for given channel dimensions and flow rate (retention time). Then, assuming an increase in the iron oxide coating thickness of 4μm/yr, we can calculate the effluent pH for every year of the mass-based expected life of the system (Table 1).

Table 1. Estimated effluent pH for an open limestone drain calculated using Eq. 17. The treatment system is predicted to fail (final pH < 6) at about 3.5 years when the effects of iron armoring are considered.

		Final pH	
Year	Coating Thickness (μm)	Without armoring	With armoring
1	0	7.0	7.0
2	4	6.9	6.7
3	8	6.7	6.2
4	12	6.5	5.7
5	16	6.2	5.2
6	20	5.8	4.7
7	24	5.4	4.1
8	28	5.0	3.6
9	32	4.6	3.2
10	36	4.2	3.0

There are two important implications to draw from the scenario in Table 1. First, even if the effect of iron armoring is ignored, the treatment system is expected to fail (pH<6) in about 5.5 years, instead of 10 years based on limestone mass. This demonstrates an inherent flaw in mass-based calculations that do not explicitly account for kinetic effects in the neutralization process. When the iron armoring is considered, the system is expected to fail in about 3.5 years, or about 65% sooner than when armoring is ignored.

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