Advanced Planning Tools for Optimization of AMD Treatment

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Abstract

Acid Mine Drainage (AMD) is gaining increasing recognition as a major water quality problem in current and former coal producing areas. Crucial to the evaluation of AMD treatment alternatives is the prediction of a measurable effect on a receiving stream. The current paper proposes a technique to estimate a pH in a receiving stream that can be expected from a treatment measure. An ongoing study being conducted by the Baltimore District of the U.S. Army Corps of Engineers is used as a case study to demonstrate this analysis.

Introduction

Contaminated water flowing from abandoned coalmines is one of the most significant contributors to water pollution in the Appalachian Mountains of the eastern United States. Acid mine drainage (AMD) occurs when groundwater comes into contact with remnant coal and rock rich in sulfide. The sulfide minerals oxidize in the presence of water and oxygen, the by-product being a highly acidic, sulfate-rich drainage (Skousen et. al 1995). AMD can have severe impacts to aquatic resources, can stunt terrestrial plant growth and harm wetlands, contaminate groundwater, raise water treatment costs, and can damage concrete and metal structures. In the Appalachian Mountains of the eastern United States alone, more than 7,500 miles of streams are impacted (Gangewere 1998).

As a result of an increased public appreciation of the environment, many federal, state and local government agencies along with grass roots organization are actively engaged in projects to identify, monitor, and treat streams that have been impacted by AMD. The success or failure of many environmental projects can be as much of a function of the success criteria as the design. Therefore, the establishment of achievable study or design goals is critical. Frequently the restoration of habitat for an aquatic target species is used as goal for the treatment effort. This is often quantified as a target pH. However, the direct calculation of pH can be problematic.

Analysis Approach

The acidity in AMD arises from free protons and the mineral acidity of dissolved metals (Hedin, 1994). pH is an abbreviation for potential of hydrogen, which is defined as the negative decimal logarithm of the molar concentration of the hydrogen ion. Overall, the product of the hydroxyl ion, OH^-, and hydrogen ion, H^+, must follow the mass action law and the resultant product of ion concentrations are always equal to 10^{-14}. For example, if enough hydrochloric acid is added to neutral water to make the solution 10^{-2} M HCl, then the hydrogen ion concentration will be 10^{-2} H^+ plus the original 10^{-7} H^+ minus the amount of H^+ that was needed to reduce the OH^- concentration to 10^{-12} resulting in approximately 10^{-2} M H^+. As a result the pH would be change from 7 to approximately 2. The 10^{-7} M of the OH^- portion is greatly reduced by the addition of the HCl. Hence the dissociation of the OH^- becomes 10^{-12} M and the H^+ portion becomes 10^{-2}. The problem gets significantly more complicated if various additional solutions are added producing unintended interactions and buffering. As if the above problems of solubility and weak acid dissociation are not enough, consideration also should be given to the effects of oxidation/reduction. The solubility product constants change with oxidation values (Barber, 1999). As a result, the direct calculation of pH in natural systems is extremely difficult.

The goal of this research is to derive a simple model for estimating the pH from the net acidity. This paper defines the net acidity as being the total acidity minus the total alkalinity. Because this relationship depends upon the mineralogy of exposed rocks in the stream channel, the precision of the model is optimized when the empirical constants are derived from data specific to the watershed of interest. However, where data are insufficient or unavailable, constants derived from an aggregate of watersheds may be used with the understanding that the prediction will not be as precise.

Model

Using data collected in several watersheds, the following empirical model was derived. This model is intended to represent equilibrium conditions.

$$pH = c_1 \max\left(1, A^2\right)^{sign(A)c_2} \quad (1)$$

Where:	A	=	Net acidity concentration, mg/L $CaCO_3$.
	$sign(A)$	=	*0*, when $A = 0$, otherwise $\lvert A \rvert / A$.
	c_1, c_2	=	Empirical model constants.

The values for the empirical model constants; c_1 and c_2, are listed below in Table 1. Data from Dents Run, Pennsylvania is shown in Figure 1. Similarly, Figure 2 shows the results of fitting the model to over 900 samples collected in over a dozen various watersheds in Pennsylvania, West Virginia and Maryland. Because alkalinity was not measured in the Dents Run samples, the empirical model constants for Dents Run were calculated using total acidity instead of net acidity. Since the majority of Dents Run samples were strongly acidic, the absence of total alkalinity data should not adversely affect the application of this model because the total acidity would be approximately equal to the net acidity. The standard error calculations indicate the refinement in prediction that can be provided with the use of data from a watershed of interest. However, if data is insufficient or unavailable to derive these constants, the data from the aggregate of watersheds provides reasonably accurate results.

Table 1. Empirical model constants

Sampled Watershed	c_1	c_2	Standard Error in Forecasted pH*
Dents Run, PA	6.1	-0.06	0.2
Muddy Creek, WV	5.7	-0.05	0.09
Deckers Creek, WV	5.3	-0.05	0.3
Average for all tested Water quality samples.	5.2	-0.05	0.4

*The standard error is the minimum absolute model error greater than 68.26% of the population.

When the net acidity is less than one, the pH is equal to the empirical constant, c_1. While a net alkaline water at a pH less than 7 may appear to be counter intuitive, it can be expected given the conditions where the data was obtained. A natural pH of ‘pure’ water can be expected to be in the 6 range due to formation or carbonic acid from atmospheric CO2 even in the absence of acid rain. For the conditions where these samples were taken, dissolved calcite can be expected to form carbonic acid and bicarbonate. As illustrated in Figure 3, the modeled relationship is also very steep near neutrality. For example, using the constants derived from the aggregate data set, a pH would change from 5.5 to 6 with the addition of less than 2.5 mg/L of alkalinity. This sensitivity could be interpreted as indicating the importance of using treatment systems, which can produce a net alkaline discharge if the capture of all the seeps is uncertain.

The alkalinity that must be added to raise the pH to the desired level can be derived by solving equation (1) for the net acidity concentration. This solution yields the following three equations.

$$A = \left(\frac{pH}{c_1} \right)^{\frac{1}{2c_2}}, \; if \;\; pH < c_1 \qquad (2)$$

$$A = 0, \; if \;\; pH = c_1 \qquad (3)$$

$$A = -\left(\frac{pH}{c_1} \right)^{-\frac{1}{2c_2}}, \; if \;\; pH > c_1 \qquad (4)$$

Example - Study Watershed Application

Dents Run is located in Elk County, Pennsylvania and has a drainage area of approximately 25.5 square miles. Dents Run is located primarily in lands owned by the State of Pennsylvania and is within the habitat range for Elk. The upper portion of the watershed is considered to be Class A wild trout stream by the Pennsylvania Fish and Boat Commission. Dents Run flows into the Bennett Branch of the Sinnemahoning Creek at the town of Dents Run. This branch then flows into the Sinnemahoning Creek and ultimately into the West Branch Susquehanna River near Keating in Clinton County, PA.

Deep and surface mining activities on this site began in the early nineteenth century and continued up until 1980. The Clarion and Lower Kittanning coal seams were extensively mined in this area (Spyker 1998). The total mined area is approximately 425 acres. The lower 4.5 miles of Dents Run is severely impacted by acid discharges from coal mines opened prior to the Surface Mining Control and Reclamation Act (SMCRA). Mine sites which drain to the Porcupine Run sub-basin contribute approximately 94% of the acid mine drainage pollution load to Dents Run but only 24% of the average daily flow (Project No. SL 161).

A recent study tested water quality samples collected in the region and found that upstream of the confluence of Porcupine Run with Dents run, the pH is approximately 6.2 while below the confluence, the pH drops to 3.5 (Spyker 1998). This study also collected macroinvertebrate data following the appropriate EPA guidance document (EPA, 1989). At the confluence with Porcupine Run, the habitat score dropped only a small amount (from 197 to 178) while several macroinvertebrate taxi were recorded upstream of the confluence and none recorded downstream. Thus, it was determined that Dents Run could support a good population of macroinvertebrates if it was unpolluted.

The Baltimore District of the U.S. Army Corps of Engineers has a long history of work in Pennsylvania. While most of the work has been with flood control projects, the Baltimore District is now broadening its mission to include environmental restoration. In late 1999, the Baltimore District began a study of possible treatment scenarios under the Section 206 Aquatic Ecosystem

Restoration Program. Eight areas have been identified as significant AMD contributors to the Dents Run watershed, shown in Figure 4.

Brook trout are used as an indicator of a larger group of species or of ecological conditions. In addition, brook trout are of particular interest to the management agencies and stakeholders. A target pH of 5.5 was selected to support this target species. While brook trout can survive in waters with a lower pH, waters with a pH of at least 5.5 are recommended for long term survival and reproduction (Penn, 1999). Following standard Corps study methodology, an incremental analysis was conducted on the possible treatment scenarios. Possible solutions to each of the eight sites have been evaluated using the net acidity - pH relationship to determine the overall study approach. It should be noted that this analysis is based on average flow conditions therefore a fluctuation is expected. The treatment techniques selected and the resulting predicted pH values are provided in Table 2. The application of these techniques should result in acid load to the watershed being reduced from 340 to 12 tons per year with the forecasted pH readings listed in Table 3.

Table 2. Selected AMD Treatment Techniques.

Treatment Site	Selected Treatment Technique	Estimated Net Acid Reduction	Final Net Acidity Load, tons/year
3888	Anoxic Limestone Drain / Open Limestone Channel	100%	0.0
3890	None	0%	0.7
3893	Regrade Surface / Alkaline Material Addition / Open Limestone Channel	90%	2.8
3895	Regrade Surface / Alkaline Material Addition	95%	1.1
1934	Regrade Surface / Alkaline Material Addition / Successive Alkalinity Production System	100%	0.0
3896/97	Regrade Surface / Alkaline Material Addition / Open Limestone Channel	95%	3.3
3898	Regrade Surface / Alkaline Material Addition	99%	0.6
Cole Draft	None	0%	3.7

Table 3. Forecasted Result of Selected AMD Treatment Techniques.

Water Quality Sampling Location	Net Acidity, Mg/L $CaCO_3$	Forecasted PH
Porcupine Run	5	5
Dents Run at confluence of Porcupine Run	2	5.6
Dents Run at confluence of Cole Draft	2.5	5.5
Mouth of Dents Run	2	5.7

In the presence of dissolved oxygen with a pH greater than 3.5, ferrous iron (Fe^{+2}) will precipitate as ferric iron (Fe^{+3}). In a similar manner, aluminum precipitates from solutions with sufficient dissolved oxygen and a pH greater than 4.2 (Fripp et. al., 1999). The seeps with the largest metal loads are in the Porcupine Run sub watershed. Since the available oxygen in Porcupine Run should be high, much of the precipitation should occur within Porcupine Run.

Example - Theoretical Application

This application of the net acidity – pH model is in the regulatory arena. The model can provide assistance in determining the amount of the alkalinity that must be added to the stream to bring it in compliance with the appropriate regulatory standards. These regulatory standards normally require that the pH of the stream be approximately equal to the pH of similar streams in un-mined watersheds. The regulatory standards for West Virginia require that the pH be no less than 6.0 and no greater than 9.0 standard units (West Virginia, 46CSR1).

A stream in a hypothetical watershed with a mineralogy similar to Dents Run has a pH of 2.5 and a mean discharge of 1000 gpm. How much alkalinity must be added to raise the pH to 6.5?

Equation (2) can be used with the Dents Run values for the empirical model constants to determine that the current net acidity is 1690 mg/L of $CaCO_3$. Equation (4) can be used with those same constants to determine that the desired net acidity is –2 mg/L of $CaCO_3$. Therefore, 1692 mg/L of $CaCO_3$ alkalinity must be added to the stream. Because the stream has a mean discharge of 1000 gpm, this concentration translates into a required treatment load of 10.2 tons of $CaCO_3$ per day.

Conclusion

This paper presents an empirical model that gives the user the ability to forecast the resulting pH caused by a reduction in net acidity concentration. The primary utility of this model is in evaluating the effect of a proposed treatment strategy on stream pH at equilibrium conditions. While this model is best applied to small watersheds with net acidity concentration and pH data, it can also be gainfully applied to watersheds with little or no calibration data. Because the empirical model makes no attempt to simulate the complex chemical reactions of solutions in natural environments, it can be applied by water quality simulation models without a significant increase in the required computational resources.

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Figures

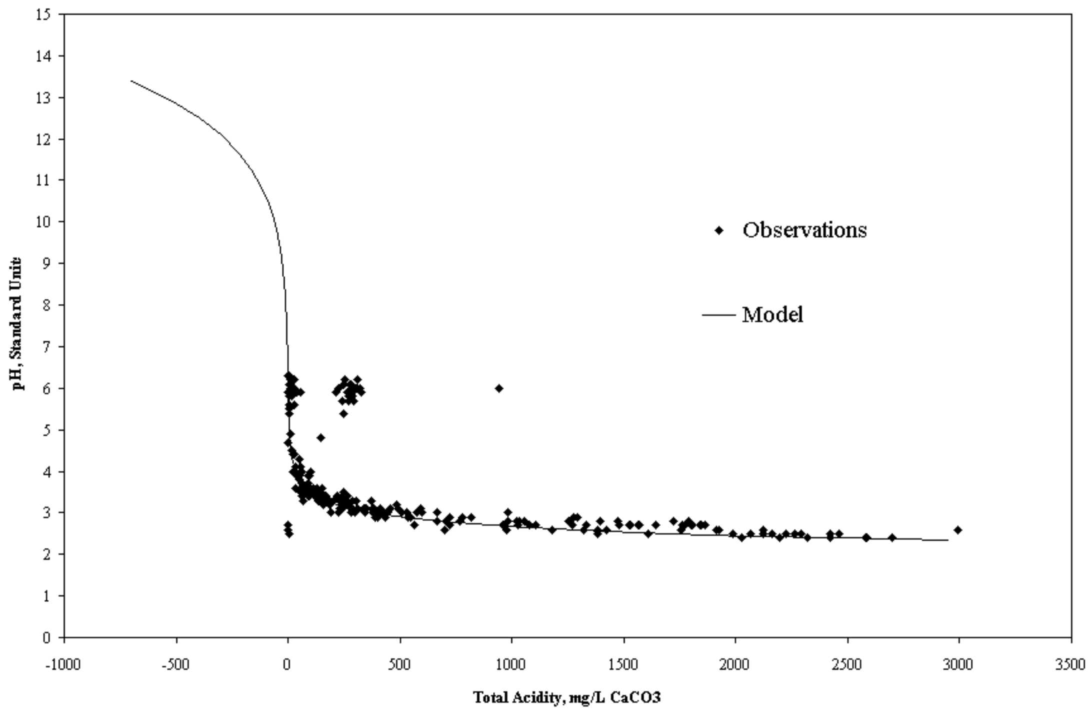

Figure 1. Dents Run pH and total acidity, mg/L $CaCO_3$, data.

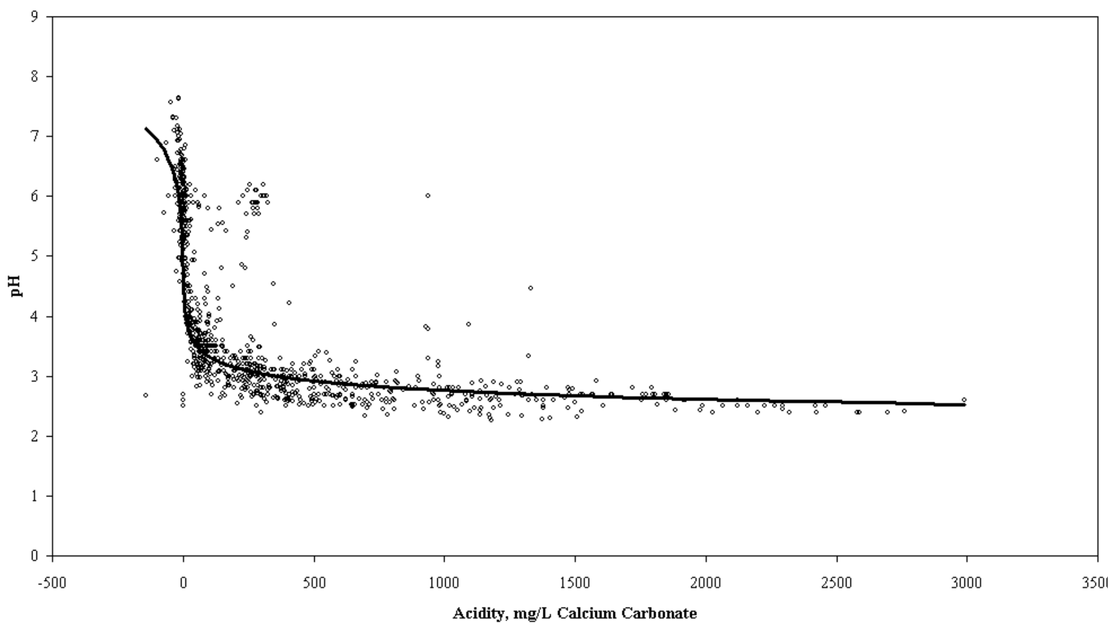

Figure 2. Unedited pH and acidity, mg/L $CaCO_3$, data from various watersheds.

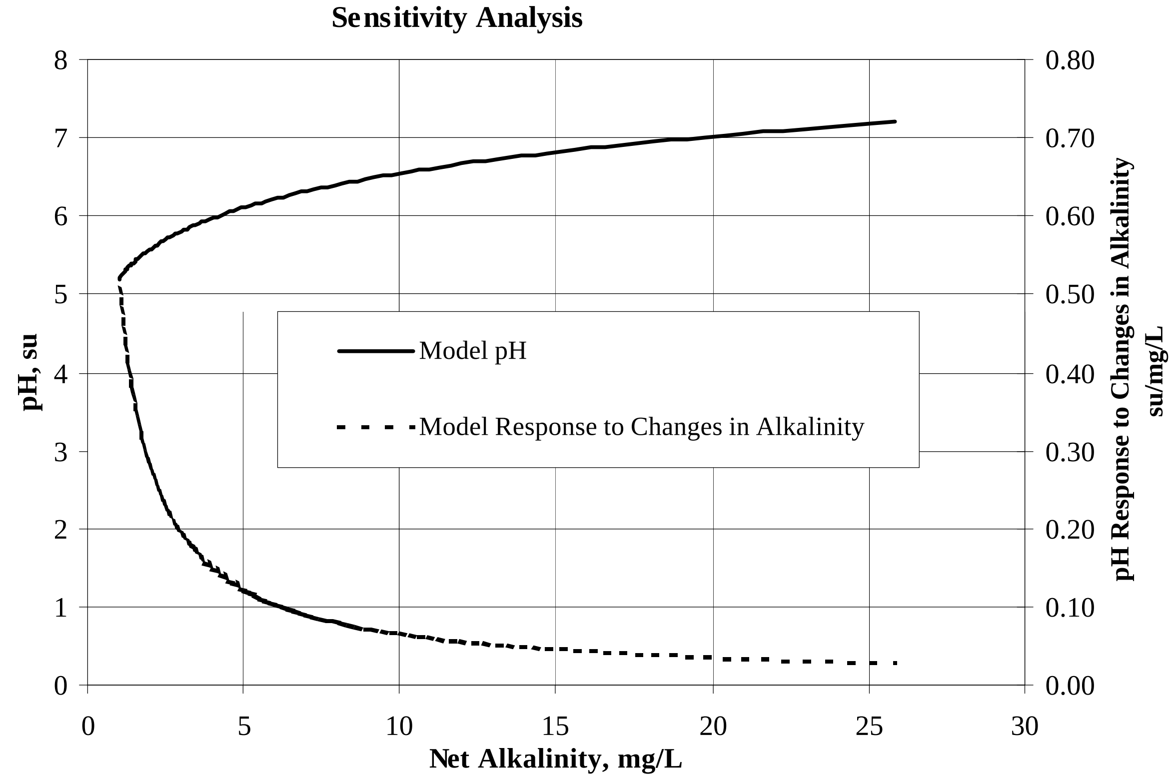

Figure 3. Sensitivity Analysis for the Empirical Net Acidity - pH Model using constants from the aggregate collection of watersheds.

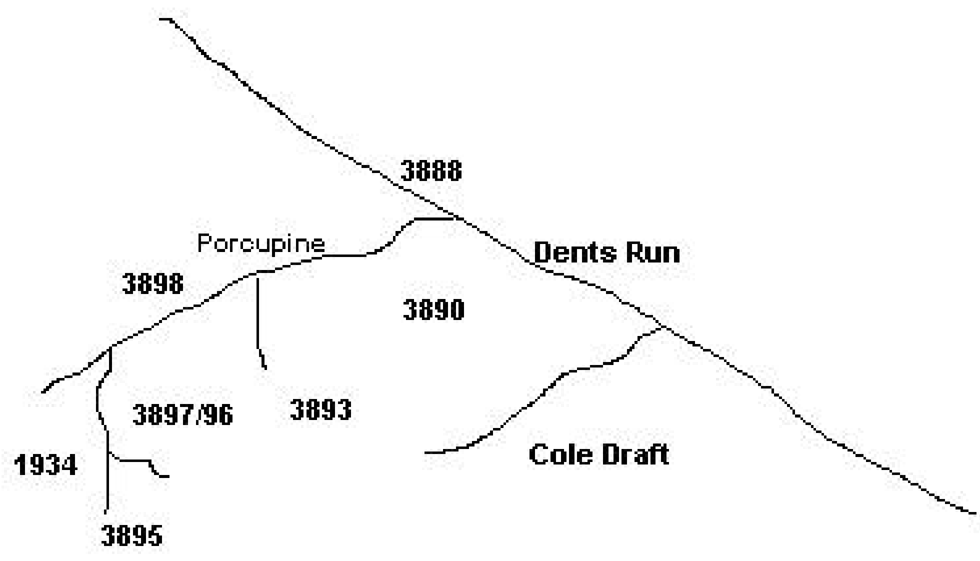

Figure 4. Schematic of Dents Run watershed