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TECHNICAL ARTICLE

Influent Water Quality Affects Performance of Passive Treatment Systems for Acid Mine Drainage

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Abstract Passive treatment of acid mine drainage (AMD) relies on biological, geochemical, and gravitational processes to neutralize acidity. Published design guidelines use sizing 'rules of thumb' based on AMD loadings at design flows. Using average performance data for 82 treatment systems, we used regression modeling to investigate the influence of influent net acidity and water loading on alkalinity generation by five treatment system types. Alkalinity generation increases with influent net acidity loading for all system types. Influent net acidity loading can be deconstructed into concentration and water loading components. In bivariate models, water loading was a predictor of alkalinity generation for all five system types but net acidity was significant only for vertical flow systems (VFs). In multivariate models using both components as performance predictors, both influenced alkalinity generation. These relationships were strongest for anaerobic wetlands (AWs), VFs, and open limestone channels; anoxic limestone drains and limestone leach beds demonstrated these influences less consistently. These results reflect the geochemical mechanisms governing the performance of limestone-based passive treatment system: solubility of limestone decreases as dissolved reaction products and pH increase.

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Introduction

Acidic waters produced by sulfide oxidation impair rivers and streams throughout the world. Such waters are commonly called acid mine drainage (AMD) because sulfides are often associated with valued minerals such as metal ores and coal, and mineral extraction often exposes associated sulfides to the ambient environment. Damaging effects of drainage from sulfide oxidation associated with mining have been described by authors for several millennia (as noted by Seal and Shanks 2008), and more recently in Asia (David 2003), New Zealand (Winterbourn et al. 2000), Europe (Casiot et al. 2009; Gray and Delaney 2008), USA (Cherry et al. 2001; Freund and Petty 2007; Courtney and Clements 2000; Kennedy et al. 2003; Soucek et al. 2000), and elsewhere. Kleinmann (1989) estimated that, in the United States alone, more than 20,000 km of streams and rivers and more than 72,000 ha of lakes and reservoirs had been adversely affected by AMD; no comparable global estimate is available.

Acidic mine drainage can be highly acidic and low in pH, and typically contains elevated concentrations of acid-soluble metals. Cravotta (2008) analyzed 140 coal mine drainages, many of which were highly acidic, for 83 constituents, including most metals and metalloids, and found that 68 elements demonstrated negative and statistically significant associations with pH. When AMD reaches a receiving stream, it is often toxic to aquatic life. Thus, several methods have been devised for treating AMD; these include 'active' systems that rely on continuing additions of alkaline chemicals to neutralize acidity, and ‘passive’ systems that principally rely on biological, geochemical, and/or gravitational processes to render sustained treatment.

Passive treatment methods for renovating AMD have developed rapidly since an early application documented by Kleinmann et al. (1983), and passive treatment applications are now employed around the world (Younger et al. 2002). Among other mechanisms, passive treatment methods commonly rely on dissolution of carbonate minerals, usually calcium carbonate supplied as limestone, to generate acid-neutralizing alkalinity, which raises pH and causes dissolved acid-soluble metals to precipitate.

Because AMD commonly contains Fe, which forms oxyhydroxides that precipitate on mineral surfaces in oxidized environments (‘armoring’) and other oxic precipitants, the most common limestone-based system types either treat anoxic waters or remove O_2 from the system waters prior to limestone contact. Anoxic limestone drains (ALDs) are buried and sealed trenches of limestone carrying anoxic waters that dissolve calcium carbonate and generate alkalinity (Turner and McCoy 1990; Watzlaf et al. 1994). Anaerobic wetlands (AWs) and vertical flow systems (VFs, also called successive alkalinity producing systems or SAPS) rely on microbial activity in biodegradable organic materials to remove O_2 from the acidic waters prior to limestone contact. AWs are open, shallow pools containing a substrate of biodegradable compost placed over or mixed with limestone (Wieder 1993; Jarvis and Younger 1999), and VFs contain open pools constructed above permeable biodegradable materials and a lower layer of limestone containing a drainage system with a standpipe that maintains standing waters in the pool (Kepler and McCleary 1994). Both VFs and AWs use biodegradable organic materials to support anaerobic sulfate reducing microbes that generate additional alkalinity and remove O_2 from the drainage waters. Limestone leach beds (LLBs) and open limestone channels (OLCs) both treat oxic waters but remain effective if the armoring that forms on the limestone, though slowing dissolution rates, remains porous. LLBs consist of limestone-filled open ponds that receive acidic waters (Black et al. 1999), while OLCs are open channels or ditches lined with limestone (Ziemkiewicz et al. 1997) and are most effective where flow velocities are sufficient to scour or hinder deposition of precipitants and suspended material on the limestone surfaces. Of these system types, LLBs and ALDs are most vulnerable to metal precipitation caused by alkalinity generation within the system; when receiving anoxic waters and effectively sealed, ALD’s primary vulnerability is to anoxic precipitants such as Al and Fe^{3+}, while both oxic and anoxic precipitants can accumulate in and foul LLBs. Because metal precipitation within both ALDs and LLBs can interfere with basic operating mechanisms, these system types are recommended only for applications where potential precipitant concentrations are low.

A fundamental task in developing AMD treatment applications is sizing, the process of designing a system capable of rendering treatment that is both economical and adequate. The sizing process seeks to assure that necessary material elements are present in quantities adequate to render effective treatment, given the expected quantity and quality of the AMD discharge and the desired environmental outcome, but are also used economically so as to limit cost. Thus, effective sizing requires that designers are able to predict the performance of a passive treatment system with some level of accuracy prior to its construction. System sizing is an essential design and development function because the selection of a treatment process is often based on evaluation of relative costs, and costs are directly affected by system size. In most applications, an evaluation of the cost to achieve the desired treatment is the ultimate determinant of whether or not a designed system is deployed.

Most published passive treatment system sizing guidelines use ‘rules of thumb’ that are based on a combination of empirical observations, experience, and scientific principles (Table 1). These rules are generally based on pollutant loading or system component sizing but do not generally consider the quality of the waters being treated—except as a contributor to pollutant loading. Considering geochemical principles likely to govern alkalinity generation by limestone-based passive treatment systems, we investigated the potential for influent water chemistry to serve as a sizing parameter by applying a multiple regression approach to an existing data set, seeking relationships that can be applied to describe system performance.

Fundamental to our approach are observations by Jage et al. (2001), who attempted to determine relationships between vertical flow system inputs, sizing, and performance using regression analysis applied to system averages. They defined system performance as the alkalinity generation, expressed as mg L^{-1} and calculated as effluent net acidity minus influent net acidity. They found that alkalinity generation increased with influent acidity (and attributed that finding to the effects of acidity on limestone solubility) and that incremental alkalinity generation rates decreased with increasing residence time of treated waters in the vertical flow systems’ limestone layer [which they attributed to the declining solubility of limestone as treatment waters became increasingly calcite saturated, as had been noted by other researchers, such as Watzlaf et al. (2000)].

Table 1 Water quality requirements and design factors for five passive treatment system types; and number of systems with performance documented by Skousen and Ziemkiewicz (2005) and Ziemkiewicz et al. (2003)

System type	Common design factors	References
Anaerobic wetland (AW)	3.5 g acidity m^{-2} day^{-1}	Hedin et al. (1994), Wildeman et al. (1993), Eger (1994), Watzlaf et al. (2000)
Anoxic limestone drain (ALD)	15 h residence time	Hedin et al. (1994), Watzlaf et al. (2004), INAP (2009)
Vertical flow wetland (VF)	15–30 cm of organic matter; 15 h residence time in limestone; 20 g acidity day^{-1} m^{-2}	Kepler and McCleary (1994, 1997), Watzlaf et al. (2000)
	25–30 g acidity day^{-1} m^{-2} for the initial system, 15 g day^{-1} m^{-2} for subsequent system(s) in series	Watzlaf et al. (2004)
	40–60 g acidity day^{-1} m^{-2} for the initial system, 1/2 to 1/3 of above for subsequent system(s) in series	INAP (2009)
Open limestone channel (OLC)	Acid load and residence time	Ziemkiewicz et al. (1997)
Limestone leach bed (LLB)	1.5 h residence time	Black et al. (1999)
	2 h residence time	Skousen and Ziemkiewicz (2005)

Methods

Passive system performance data reported by Skousen and Ziemkiewicz (2005) were analyzed. These researchers evaluated 116 passive treatment systems of eight types in eight states. Each system was monitored for influent and effluent flow and water quality over an extended period; these parameters were reported as system averages. Flows were measured by a bucket and stopwatch, weirs, or flow meters; water samples were analyzed for pH, acidity and alkalinity, and metal concentrations by certified laboratories. Because laboratories generally measure acidity using the 'hot acidity' technique (US EPA 1983), reported acidity values are equivalent to the quantity that is commonly called 'net acidity' (Kirby and Cravotta 2005). A sizing parameter was reported for each monitored system, either tonnes (t) of limestone or surface area (m^2). Earlier performance data for most of these same systems were also reported by Ziemkiewicz et al. (2003), who also described a small number of systems not included in the latter paper. Performance data for five system types that rely on limestone dissolution as a primary treatment mechanism were evaluated for this study: AWs, ALDs, VFs, OLCs, and LLBs.

For systems reported in both papers, the 2005-reported performance data were used in this analysis. For those few systems reported only by Ziemkiewicz et al. (2003), these performance data were used. Systems exhibiting zero or negative alkalinity generation, an indicator of improper functioning, and systems receiving net-alkaline influent were excluded from the analysis. One LLB system reported only by Ziemkiewicz et al. (2003) that otherwise met the conditions for this analysis, WV-36c, was excluded because its extremely short retention time, 0.3 h, would have otherwise caused an essential modeling variable (ln-transformed water loading) to become highly skewed. In addition to the parameters reported in the source publications, we calculated additional system parameters using those data.

Alkalinity generation was calculated for each system as a concentration by calculating the difference between effluent and influent acidity, and on a system-size basis using either surface area (m^2) or mass of limestone (t), depending on system type and source data. Influent acidity loading was calculated for each system using the same sizing parameter. Water loading, defined as reported flow divided by the system-sizing parameter, was calculated for each system.

Separately for each of the five system types, size-based alkalinity generation was modeled as a function of influent acidity loading as the first stage of analysis. Influent acidity loading was then decoupled into two components: influent acidity and influent water loading. Alkalinity generation was modeled as a function of these two parameters in two phases: first, two bivariate models were constructed using both of the influent acidity loading components as predictor variables; and then multivariate models were constructed using both components as predictors. In constructing models, all variables were log-transformed as needed to define variables with distributions that more closely approximated a normal distribution than the non-transformed variables, which were typically skewed. Modeling was performed as linear regressions using the "Fit Model" function of JMP 7.0 statistical software (© 2007, SAS Institute Inc., Cary NC).

The models resulting from these analyses were evaluated for their potential utility in describing passive treatment system design performance considering standard statistical parameters such as coefficient of determination (R^2) and p-values.

Results

For all five system types, bivariate models of size-based alkalinity generation as a function of influent acidity loading (Table 2; Fig. 1) are highly significant ($p < .0001$). All of the models except ALDs yield coefficients of determination (R^2) of >0.7. R^2 values are highest for AWs and OLCs at >0.9.

Table 3 reports bivariate alkalinity generation prediction models, with the two influent acidity loading components treated separately as predictor variables. Water loading is a significant predictor of alkalinity generation for all system types, but influent acidity is significant (at $p < .05$) as a performance predictor for only the VF systems and explained less than 10% of performance variation for ALDs, OLCs, and LLBs.

Table 4 and Fig. 2 present results of multivariate models that used both influent acidity loading components (influent acidity and water loading) to predict system performance. The resulting models for all five system types are statistically significant; and the model coefficients for both independent variables are uniformly statistically significant ($p < .05$) and positive. None of the interactions between the two predictor variables were statistically significant.

Discussion

These results confirm two fundamental mechanisms that govern limestone-based passive treatment system performance: (a) alkalinity generation varies positively with influent acidity, and (b) alkalinity generation varies positively with water loading. Both of these mechanisms are consistent with well-known geochemical mechanisms.

The accumulation of mineral dissolution reaction products in solution depresses mineral dissolution rates; experimental observations demonstrate that limestone dissolution, although also affected by solution chemistry, conforms to this pattern (Morse and Arvidson 2002). Water loading is positively related to alkalinity generation in all models in which water loading is a variable, a relationship that reflects the fact that water movement through the system removes dissolved calcite; greater rates of flow remove dissolved calcite more rapidly, allowing less inhibition of carbonate dissolution via accumulation of reaction products in solution. All bivariate models with log-transformed water loading as a system performance predictor generate positive coefficients that are statistically significant ($p < .05$) (Tables 3, 4).

Although water retention time was not modeled directly, the water loading variable is inversely related to limestone retention time for each system type; this relationship is represented by Fig. 3 (left) for ALDs using retention times reported in the original data sources. Figure 3 (right) represents the response of alkalinity generation, predicted as a function of water loading by the bivariate model (Table 3) to retention time for each of the 34 ALD systems; the resulting response is similar to that demonstrated by Watzlaf et al. (2000) empirically. This result is also consistent with results reported by Jage et al. (2001), who found a positive and logarithmic response of alkalinity generation to limestone-layer retention time in VF systems. The same functional form is incorporated in the multivariate modeling forms of Table 4.

At the sub-circumneutral pHs represented by the passive systems' influent waters, protons enhance hydration and detachment of calcium carbonate ions from calcite surfaces (Plummer et al. 1978; Shiraki et al. 2000) causing limestone solubility to be inversely related to pH (Morse and Arvidson 2002). Influent acidity and loading are positively related to alkalinity generation in all models in which they were included, although only one of the five acidity bivariate models was statistically significant ($p < .05$). Positive relationships of influent acidity with alkalinity generation reflect increasing solubility of calcite with decreasing pH. Influent pH itself is inversely and significantly related to influent acidity in all of these data sets, as expected.

Influent acidity, as opposed to pH, was used as a system performance predictor variable despite the fact that limestone solubility is directly affected by pH. Multivariate system performance models constructed with influent pH and water loading as predictor variables were uniformly less satisfactory than those reported in Table 4 (data not shown): all R^2 values were lower, and the influent pH

Table 2 Models describing alkalinity generation, on a system size basis, as a function of acidity loading for each of five primary AMD passive treatment system types

System type	n	a	b	R^2	p-Value
AW	10	−0.266151	0.8708899	0.933	<.0001
ALD	34	1.3044657	0.6243566	0.475	<.0001
VF	13	0.8933616	0.7889751	0.830	<.0001
OLC	10	−0.556281	0.9344967	0.925	<.0001
LLB	15	0.4063925	0.7685494	0.734	<.0001

All models are of a form of: $\ln(y) = a + b \ln(x)$, where x = influent acidity, expressed as g $\text{day}^{-1}\ \text{t}^{-1}$ for ALDs, OLCs, and LLBs, and as g $\text{day}^{-1}\ \text{m}^{-2}$ for AWs and VFs; and y = alkalinity generation, expressed as the same units. Models can also be expressed as $y = \exp[a + b \ln(x)]$ where exp is an exponential function of mathematical constant e. In the table above, n is the number of systems used for model development

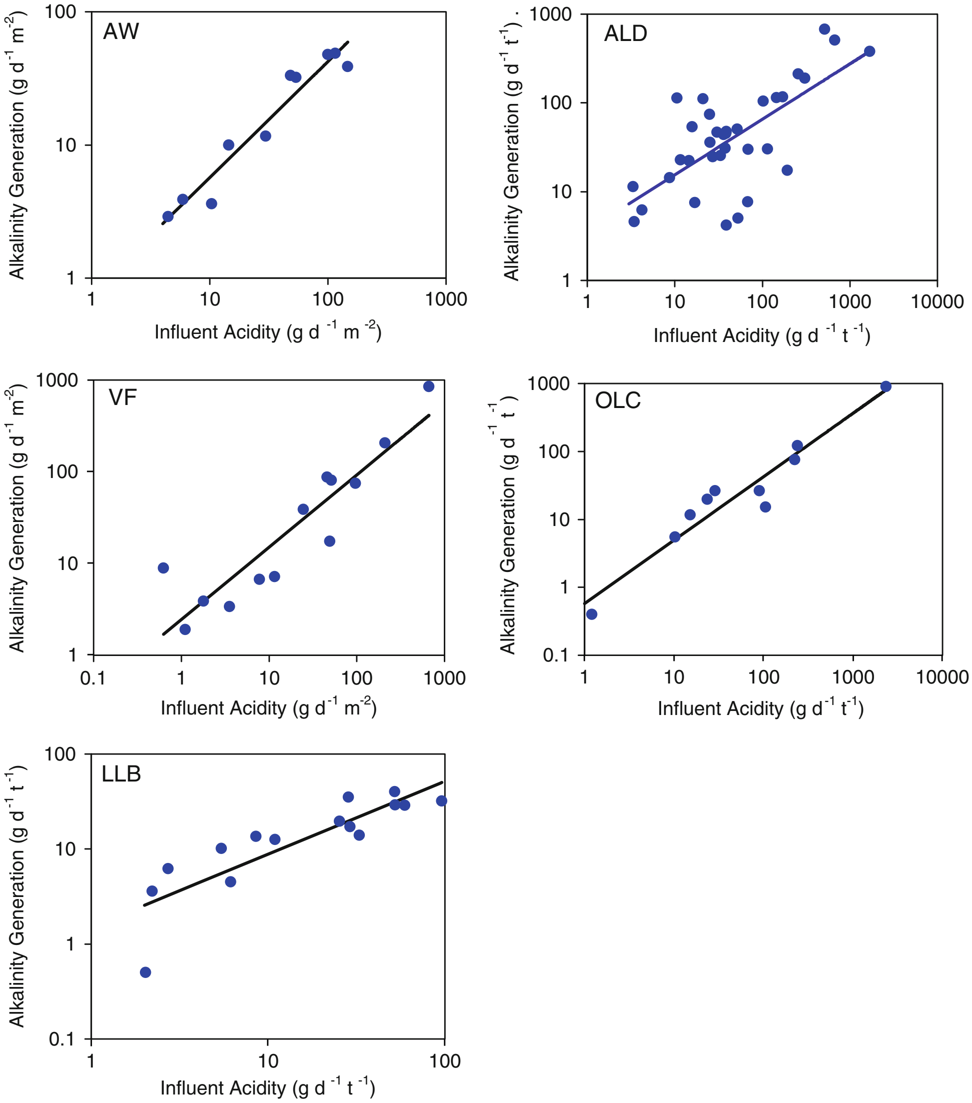


Fig. 1 Graphic representations of the system performance models listed in Table 2

Table 3 Bivariate models of alkalinity generation as functions of water loading and as a function of influent acidity

Type	*a*	*b*	R^2	*p*-Value
Water loading				
AW	−1.240402	+0.8131076	0.496	0.023
ALD	−0.537724	+0.8421766	0.578	<.0001
VF	−2.143406	+1.1213882	0.678	0.0005
OLC	−1.676041	+0.7535827	0.578	0.011
LLB	−0.30592	+0.6105266	0.472	0.005
Influent acidity				
VF	−2.027582	+1.0266687	0.459	0.011

All models are of a form of: $\ln(y) = a + b \ln(x)$, where x = water loading (L day^{-1} t^{-1} for ALDs, OLCs, and LLBs, and as L day^{-1} m^{-2} for AWs and VFs) (above), and x = influent acidity (mg L^{-1}) (below); and y = alkalinity generation, expressed as g day^{-1} t^{-1} for ALDs, OLCs, and LLBs, and as g day^{-1} m^{-2} for AWs and VFs. Only models with statistically significant parameter estimates ($p < .05$) are listed

coefficient was not significant at $p < .05$ for three of the five pH-based multivariate models. These results reflect the fact that the metals contributing to solution acidity generate protons when hydrolyzed (Hedin et al. 1994); although influent acidity and pH were positively correlated for all system types, acidity varied widely between some waters with similar pH (Fig. 4, left). The multivariate models of Table 4 use influent acidity as a performance predictor; of these five models, the least gain in R^2, relative to the corresponding pH-based multivariate model was achieved by ALDs, the system for which influent acidity proved least satisfactory as a predictor variable.

As with water loading, the functional form for the influent acidity component of the multivariate prediction models (Table 4) is consistent with geochemical mechanisms influencing limestone dissolution rates. In order to demonstrate this correspondence graphically, we calculated a functional relationship between influent acidity and pH

Table 4 Multivariate passive system performance prediction models for five passive system types

Type	Model coefficients			Coefficient *p*-values			Model R^2	(Adjusted R^2)
	a	*b*	*c*	*a*	*b*	*c*		
AW	−6.244338	+0.967478	+0.778738	.0001	<.0001	.0001	0.949	(0.934)
ALD	−2.578941	+0.903297	+0.303996	0.0208	<.0001	0.0245	0.642	(0.619)
VF	−4.420872	+0.904008	+0.654413	0.0026	0.0101	0.0007	0.839	(0.807)
OLC	−6.838740	+0.972224	+0.841922	0.0004	0.0007	0.0101	0.933	(0.915)
LLB	−4.757087	+0.907051	+0.614133	0.0009	<.0001	0.0005	0.813	(0.782)

All models are of form: Ln (y) = $a + b \ln(x_1) + c \ln(x_2)$, where y = alkalinity generation, x_1 = water loading, and x_2 = influent acidity, with all units as in Table 3

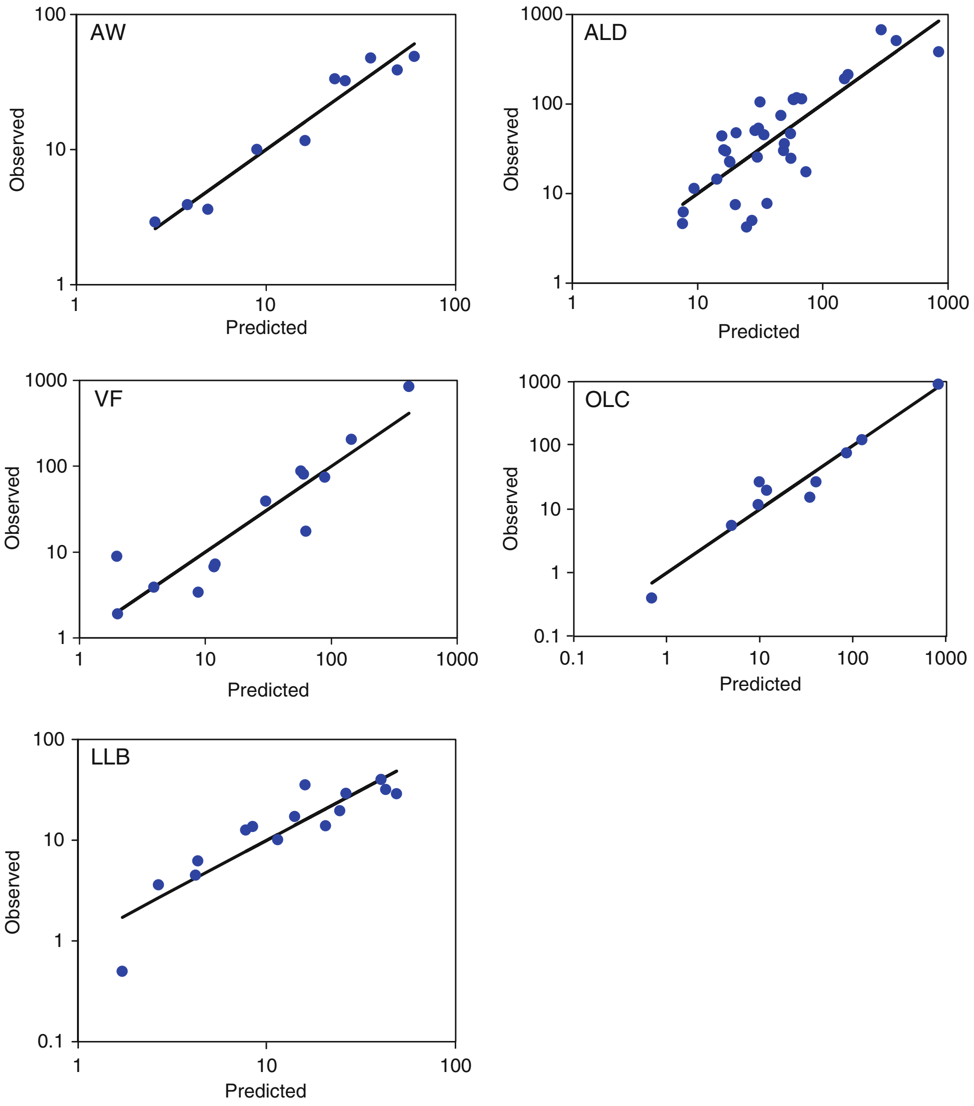
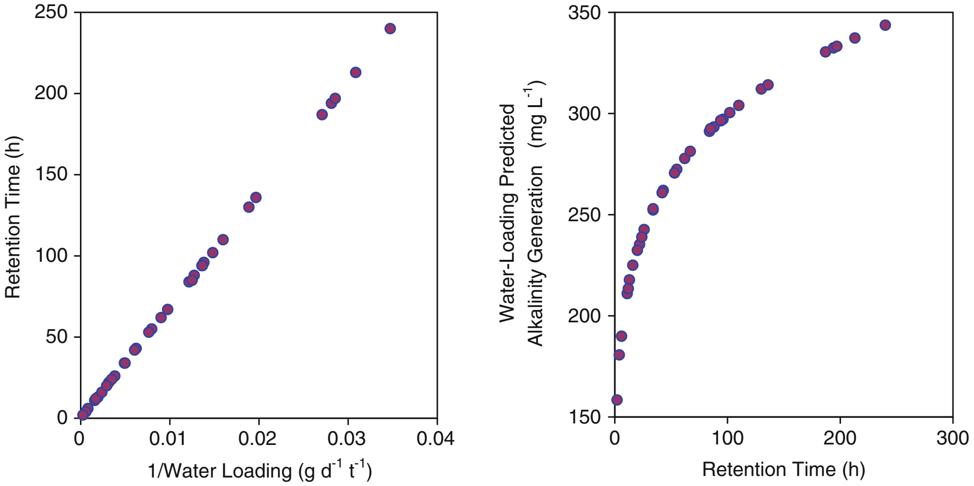


Fig. 2 Predicted size-based alkalinity generation, using models of Table 4, versus observed values; units are g day^{-1} t^{-1} for ALD, OLC, and LLB; and g day^{-1} m^{-2} for AW and VF. *Solid lines* represent 1:1 correspondence

(Fig. 4, left), and used that relationship to express the dependence of size-based alkalinity generation on influent acidity transformed to an 'influent acidity-equivalent pH' at median water loadings (148 L day^{-1}m^{-2} for AW and VF, 125 L day^{-1}t^{-1} for ALD, OLC, and LLB) using the multivariate model forms (Fig. 4, center and right); the resulting function illustrates geochemical relationships that are similar in form with the well-established geochemical effect of pH on calcite dissolution rates (Fig. 5; see also Morse and Arvidson 2002).

For all five system types, the multivariate prediction model that includes the two components of influent acidity

Fig. 3 (*Left*) Relationship of water loading variable to retention time (hours), as listed in the source data for each of the 34 ALD systems; (*Right*) the response of water-loading predicted alkalinity generation for each of the 34 ALD systems, expressed as a concentration, to retention time



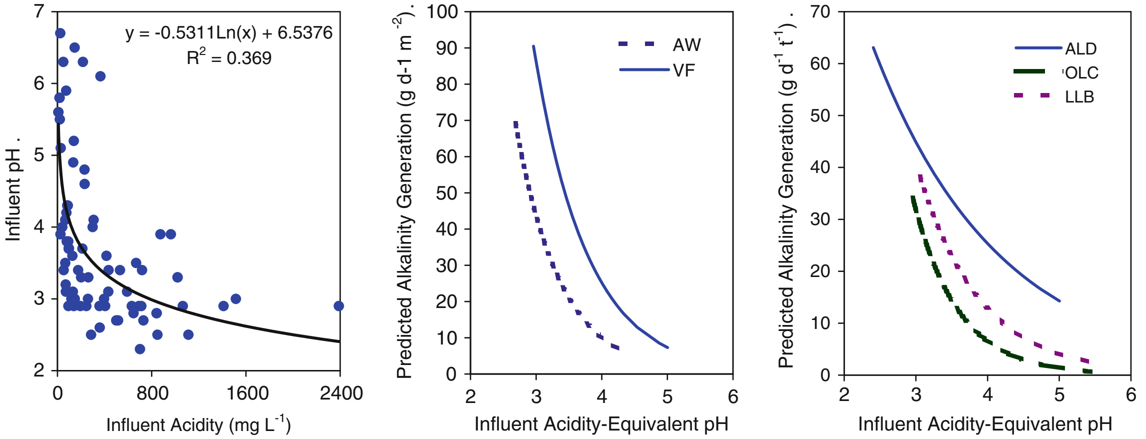


Fig. 4 (*Left*) Influent acidity versus influent pH for all of the 82 passive treatment systems, and the functional form used to generate influent acidity-equivalent pH values; (*Center* and *Right*) the response of size-based alkalinity generation to influent acidity-equivalent pH at median water loadings

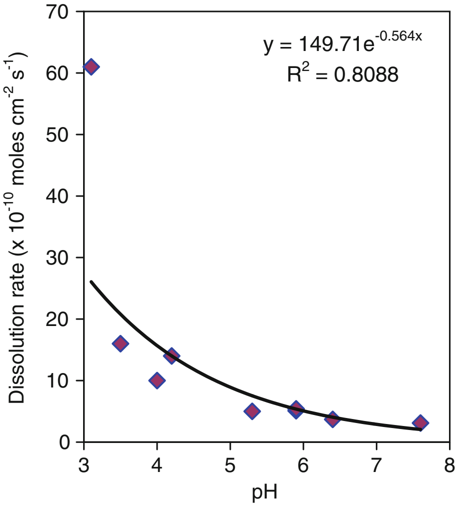


Fig. 5 Effect of pH on calcite dissolution rates in water from Shiraki et al. (2000), with exponential functional form fitted by the authors

loading (Table 4) produced a higher R^2 than the corresponding bivariate model using only influent acidity loading as a performance predictor (Table 2); in some cases (AW, VF, OLC), only marginal improvements were noted. The multivariate R^2 increases were greatest for the two system types characterized most poorly by the bivariate models, LLBs and ALDs; the increase was greatest for ALDs, the system type whose performance was predicted least accurately by the bivariate model.

By all measures, the multivariate performance prediction model was least adequate for ALDs: this model generated the lowest R^2 value; and, of the 10 multivariate predictor-variable coefficients of Table 4, its influent acidity coefficient had the highest *p*-value and thus, the lowest level of statistical significance. We believe this is largely due to the fact that two components of acidity, Al and Fe^{3+}, degrade ALD performance (Watzlaf et al. 2000), in contrast to the models' inherent assumption that all influent acidity components will cause system performance to improve. In addition, a third component, Fe^{2+}, is not expected to generate protons in the anoxic conditions that prevail within ALDs. Although common ALD design guidelines (e.g. Hedin et al. 1994, Hedin 2002; Skousen et al. 2000; Watzlaf et al. 2004) recommend that these systems be applied only to treat waters with low concentrations of potential anoxic precipitants, AMD water chemistry typically varies, recommended guidelines are not always followed, and even low levels of anoxic precipitants can impair system performance over time. Use of influent pH and ln-transformed water loading as performance predictors for ALDs, an alternative approach that avoids these complications, generates a model with an R^2 (0.622) approaching that of the primary model reported in Table 4, but with a pH coefficient that is not statistically significant ($p = .0647$). LLBs, for which the models also performed poorly relative to the remaining three system types, also experience performance degradation when influent waters contained metals that are subject to precipitation with increasing solution pH. Had the WV-36c LLB system been included in the modeling procedure, R^2 values for all statistically significant LLB models, as reported in Tables 2, 3, and 4, would have increased but at the expense of statistical validity due to WV-36c's effect on the distribution of the ln-transformed water loading variable.

We interpret these results as evidence that influent water quality can be usefully considered as a design parameter for passive treatment systems. This result is consistent with findings for VF systems by Rose and Dietz (2002) and Rose (2004) (who found that net alkalinity added varies positively with influent acidity) and with Watzlaf et al. (2004) and INAP (2009)(who found that VF systems treating waters discharged from prior VF systems in a treatment sequence will generate less alkalinity than the initial VF in that sequence). We interpret these results as a more general statement of those findings.

We used acidity, as commonly measured, as the water-quality variable of concern considering limitations of the source data, which did not list metal concentrations. However, geochemical mechanisms governing passive-system operations suggest that other water quality measures may give improved results when used to predict system performance. For example, Jage et al. (2001) defined the component of acidity derived from constituents other than Mn, which they termed as non-manganese acidity (non-Mn acidity) and found that inclusion of non-Mn acidity in VF alkalinity-generation prediction models improved those models' R^2 values, compared to corresponding models that included influent acidity, conventionally defined, as a predictor. Rose (2004) also used non-Mn acidity as a VF system performance predictor. The rationale for using non-Mn acidity as predictor is that Mn oxidizes to precipitant forms rapidly only at pH's greater than the practical maximum ($\approx$7.0–7.5) that most passive treatment systems are able to achieve (Skousen et al. 2000); therefore, Mn is not oxidized effectively and thus does not generate protons to accelerate $CaCO_3$ dissolution. Given that Al and Fe^{3+} are known to detract from performance of ALDs and that LLBs respond poorly to the presence of any precipitant metals, it is possible that use of modified influent-acidity measures for these system types would allow improved performance prediction. Similarly, use of a modified acidity measure that excludes Fe^{2+}, which does not generate additional protons in the absence of oxygen, may prove useful in systems such as ALDs where primary treatment occurs under anoxic conditions.

These results provide evidence that influent water quality influences passive treatment system performance, but the models reported here are not suggested or presented as general models to be applied universally to predict passive treatment system performance. The exponential model-form predictions (i.e. $y = e^{[a+b\ln(x_1)+c\ln(x_2)]}$) show greater variance from actual performance, especially for higher influent acidity loadings, than is evident from the graphic representations of the ln-transformed model-form results (Fig. 2), demonstrating that factors in addition to influent acidity and water loadings exert major influences on system performance. This has been observed by others, including Rose (2006). Consideration of geochemical mechanisms also suggests that elevated Ca^{++} will depress alkalinity generation in limestone-based systems receiving pretreated waters, such as those discharged from an ALD or an initial-stage VF. It is likely that more robust and general models could be developed through application of system-specific modeling procedures applied to larger performance data sets.

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References

Black C, Ziemkiewicz P, Skousen J (1999) Construction of a limestone leach bed and preliminary water quality results in Beaver Creek. Proceedings of 20th WV surface mine drainage task force symposium West Virginia University, Morgantown

Casiot C, Egal M, Elbaz-Poulichet F, Bruneel O, Bancon-Montigny C, Cordier M, Gomez E, Aliaume C (2009) Hydrological and geochemical control of metals and arsenic in a Mediterranean river contaminated by acid mine drainage (the Amous River, France); preliminary assessment of impacts on fish (*Leuciscus cephalus*). Appl Geochem 24:787–799

Cherry D, Currie R, Soucek D, Latimer H, Trent G (2001) An integrative assessment of a watershed impacted by abandoned mined land discharges. Environ Pollut 111:377–388

Courtney L, Clements W (2000) Sensitivity to acidic pH in benthic invertebrate assemblages with different histories of exposure to metals. J N Am Benthol Soc 19:112–127

Cravotta CA (2008) Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 1: constituent quantities and correlations. Appl Geochem 23:166–202

David C (2003) Establishing the impact of acid mine drainage through metal bioaccumulation and taxa richness of benthic insects in a tropical Asian stream (the Philippines). Environ Toxicol Chem 22:2952–2959

Eger P (1994) Wetland treatment for trace metal removal from mine drainage: the importance of aerobic and anaerobic processes. Water Sci Technol 29:249–256

Freund J, Petty JT (2007) Response of fish and macroinvertebrate bioassessment indices to water chemistry in a mined Appalachian watershed. Environ Manage 39:707–720

Gray N, Delaney E (2008) Comparison of benthic macroinvertebrate indices for the assessment of the impact of acid mine drainage on an Irish river below an abandoned Cu-S mine. Environ Pollut 55:31–40

Hedin R (2002) Passive treatment of polluted mine waters. In: Younger P, Banwart L, Hedin R (eds) Mine water: hydrology, pollution, remediation, vol 5. Kluwer, Dordrecht, pp 311–396

Hedin R, Nairn R, Kleinmann R (1994) Passive treatment of coal mine drainage. US Bureau of Mines IC 9389, US Dept of the Interior, Pittsburgh, p 35

International Network for Acid Prevention (2009) Global acid rock drainage guide. Accessed 4 Oct 2009 at http://www.gardguide.com

Jage C, Zipper C, Noble R (2001) Factors affecting alkalinity generation by successive alkalinity producing systems: regression analysis. J Environ Qual 30:1015–1022

Jarvis A, Younger P (1999) Design, construction and performance of a full-scale compost wetland for mine-spoil drainage treatment at Quaking Houses. Water Environ Manage 13:313–318

Kennedy A, Cherry D, Currie R (2003) Field and laboratory assessment of a coal processing effluent in the Leading Creek Watershed, Meigs County, Ohio. Arch Environ Con Tox 44(3): 324–331

Kepler D, McCleary E (1994) Successive alkalinity-producing systems (SAPS) for the treatment of acidic mine drainage. In: International Land Reclamation and Mine Drainage Conf, US Bureau of Mines SP 06A-94, US Dept of the Interior, Pittsburgh, pp 195–204

Kepler D, McCleary E (1997) Passive aluminum treatment successes. In: Proceedings of 18th WV surface mine drainage task force symposium, West Virginia University, Morgantown

Kirby C, Cravotta C (2005) Net alkalinity and net acidity 1: theoretical considerations. App Geochem 20:1920–1940

Kleinmann R (1989) Acid mine drainage. Eng Min J 190:16I–16N

Kleinmann R, Tiernman T, Selch J, Harris R (1983) A low cost low maintenance treatment system for acid mine drainage using Sphagnum moss and limestone. Proceedings of symposium on surface mining, hydrology, sedimentology, and reclamation. University of Kentucky, Lexington, pp 241–245

Morse J, Arvidson R (2002) The dissolution kinetics of major sedimentary carbonate minerals. Earth Sci Rev 58:51–84

Plummer LN, Wigley TML, Parkhurst DL (1978) The kinetics of calcite dissolution in CO_2-water systems at 5° to 60° C and 0.0 to 1.0 atm CO_2. Am J Sci 278:179–216

Rose AW (2004) Vertical flow systems—effects of time and acidity relations. Proceedings of 2004 National Meeting of the American Society of Mining and Reclamation, Morgantown, pp 1595–1615

Rose AW (2006) Long-term performance of vertical flow ponds—an update. Proceedings of 2006 National Meeting of the American Society of mining and reclamation, St. Louis, pp 1704–1716

Rose AW, Dietz JM (2002) Case studies of passive treatment systems: vertical flow systems. Proceedings of 2002 National Meeting of the American Society of mining and reclamation, Lexington, pp 776–797

Seal RR, Shanks WC (2008) Sulfide oxidation: insights from experimental, theoretical, stable isotope, and predictive studies in the field and laboratory. Appl Geochem 23:101–102

Shiraki R, Rock PA, Casey WH (2000) Dissolution kinetics of calcite in 0.1 M NaCl solution at room temperature: an atomic force microscopic (AFM) study. Aquat Geochem 6:87–108

Skousen J, Ziemkiewicz P (2005) Performance of 116 passive treatment systems for acid mine drainage. Proceedings of National Meeting of the American Society of mining and reclamation, Breckinridge, pp 1100–1133

Skousen J, Sexstone A, Ziemkiewicz P (2000) Acid mine drainage control and treatment. In: Barnhisel R, Daniels W, Darmody R (eds) Reclamation of drastically disturbed lands. American Society of Agronomy, Madison, pp 131–168

Soucek D, Cherry D, Currie R, Latimer H, Trent G (2000) Laboratory to field validation in an integrative assessment of an acid mine drainage-impacted watershed. Environ Toxicol Chem 19:1036–1043

Turner D, McCoy D (1990) Anoxic alkaline drain treatment system, a low cost acid mine drainage treatment alternative. In: Proceedings of National Symposium on Mining, University of Kentucky, Lexington, pp 73–75

US EPA (Environmental Protection Agency) (1983) Method 305.1, acidity (Titrimetric). In: Methods for chemical analysis of water and wastes. US Environmental Protection Agency EPA/600/4-79-020

Watzlaf G, Kleinhenz J, Odoski J, Hedin R (1994) Performance of the Jennings Center anoxic limestone drain. Abstract, US Bureau of Mines SP 06B-94, US Dept of the Interior, Pittsburgh, p 427

Watzlaf G, Schroeder K, Kairies C (2000) Long-term performance of anoxic limestone drains. Mine Water Environ 19:98–110

Watzlaf G, Schroeder K, Kleinmann R, Kairies C, Nairn R (2004) The passive treatment of coal mine drainage. DOE/NETL-2004/1202, US Dept of Energy, ftp://ftp.netl.doe.gov/pub/Watzlaf/, 72 pp

Wieder R (1993) Ion input/output budgets for wetlands constructed for acid coal mine drainage treatment. Water Air Soil Pollut 71:231–270

Wildeman T, Gusek J, Brodie G (1993) Wetland design for mining operations. Bitech Publishers LTD, Richmond, p 408

Winterbourn M, McDiffett W, Eppley S (2000) Aluminium and iron burdens of aquatic biota in New Zealand streams contaminated by acid mine drainage: effects of trophic level. Sci Total Environ 254:45–54

Younger P, Banwart L, Hedin R (2002) Mine water: hydrology, pollution, remediation. Kluwer, Dordrecht, p 442

Ziemkiewicz P, Skousen J, Brant D, Sterner P, Lovett R (1997) Acid mine drainage treatment with armored limestone in open limestone channels. J Environ Qual 26:560–569

Ziemkiewicz P, Skousen J, Simmons J (2003) Long-term performance of passive acid mine drainage treatment systems. Mine Water Environ 22:118–129