

GENERATION OF 400-500 MG/L ALKALINITY IN A VERTICAL ANOXIC LIMESTONE DRAIN¹

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Abstract: Alkalinity generation in a vertical anoxic limestone drain (VALD) at an abandoned coal mine discharge near Hartshorne, Oklahoma was evaluated. The VALD consists of a 9-m² abandoned vertical air shaft filled with approximately 22 m of >90% CaCO₃ limestone overlying approximately 34 m of dolomitic stone. The VALD and a downstream passive treatment system were designed to treat a net-acidic discharge (~40 L/min) characterized by elevated concentrations of metals (Fe 765 mg/L; Mn 18 mg/L; Na 1900 mg/L), anions (Cl⁻ 225 mg/L; SO₄²⁻ 7800 mg/L), with pH 5.4 and net-acidity 1400 mg/L. System construction was completed in late 2005, but discharge from the VALD did not occur until January 2007 due to a prolonged regional drought. Upon initial discharge, alkalinity concentrations from the VALD outflow were 550±14 mg/L. During the first year of operation, alkalinity concentrations consistently remained >400 mg/L. The effects of elevated pCO₂, mine water ionic strength, detention time, and other factors impacting alkalinity concentrations exiting the VALD were assessed. It appears that multiple factors, especially the brackish nature of these particular mine waters, influence treatment effectiveness. In addition, the down-gradient 12-cell passive treatment system is effectively removing metals and discharging net alkaline waters to the receiving stream.

Additional Key Words: acid mine drainage, carbonate chemistry, ionic strength, geochemical modeling

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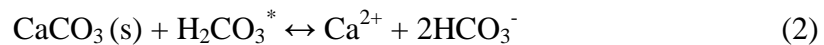
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Introduction

Anoxic limestone drains (ALDs) are typically used to treat mine drainage discharges with $\text{pH} > 4$ and low ($\sim < 1 \text{ mg/L}$) concentrations of Fe^{3+} , Al, and dissolved oxygen (DO) (e.g., Watzlaf et al., 2004) and usually consist of buried beds of high ($> 90\%$) calcite limestone. As mine water flows through an ALD under anoxic conditions, limestone dissolves neutralizing proton acidity and producing dissolved carbon dioxide (Equation 1, where $\text{H}_2\text{CO}_3^* = \text{CO}_2(\text{aq}) + \text{H}_2\text{CO}_3^0$) which further reacts with calcite to generate bicarbonate alkalinity (Equation 2) (e.g., Younger et al., 2002; Cravotta 2003).



Several factors affect the generation of alkalinity from these reactions; including partial pressure of carbon dioxide (P_{CO_2}), temperature, and ionic strength of the mine waters. The rates and extent of limestone dissolution are controlled by reactions between water, calcite, and carbon dioxide governed by the carbonate system (Kaufmann and Dreybrodt, 2007). It has been found that the solubility of carbonate minerals is affected by P_{CO_2} , which may become elevated in the closed atmosphere of ALDs as limestone dissolves (Equation 1). In addition, typical untreated mine drainage waters have P_{CO_2} of 10^{-1} atm or greater (Younger et al., 2002) thus influencing both kinetics and solubility. Increases in P_{CO_2} in an ALD cause an increase in the solubility of calcite, thus increasing the concentration of bicarbonate alkalinity in the system (Watzlaf et al., 2004).

Temperature also affects the solubility of calcite, particularly in the range of 5° to 25°C . The solubility product (K_{sp}) of calcite can decrease 20 to 25% in this temperature range (MacKenzie and Lerman, 2006). However, temperature of any specific mine drainage water is relatively constant and is not expected to affect the solubility of calcite in an ALD to any considerable extent. In addition, the buried nature of groundwater-fed ALDs serves to dampen any temperature fluctuation.

Ionic strength, however, can cause a considerable change in the K_{sp} of calcite (Stumm and Morgan, 1996). Ionic strength has also been shown to affect reaction rates between ions (Morel and Hering, 1993) and surface thermodynamics (Walther, 2005). In addition, elevated concentrations of charged molecules in the water allows for the formation of ion pairs (e.g.,

CaSO_4^0 , MgSO_4^0 , etc.). The removal of free Ca^{2+} and Mg^{2+} ions from solution through ion pairing would promote further dissolution of calcite and/or dolomite (Drever, 1997). Although ionic strength is typically elevated in mine drainage above values found in natural waters, the effects of ionic strength on passive treatment effectiveness have not been extensively evaluated.

In this study, alkalinity data collected from the outflow of a vertically-oriented ALD (VALD) were evaluated with respect to detention time, P_{CO_2} and ionic strength. In the first year of operation, the VALD produced greater alkalinity concentrations than reported in previous studies (e.g., Nairn et al 1992, Hedin et al., 1994, Watzlaf et al., 2000; Younger et al, 2002, Cravotta 2003; Santomartino and Webb 2007). This paper represents an initial effort to assess the early performance of this particular system.

Methods

Through a cooperative effort of the Office of Surface Mining Reclamation and Enforcement, Oklahoma Conservation Commission and others, a passive treatment system was constructed in late 2005 (Whitlock/Jones 145 CSI AML Project) to treat an abandoned (ca. 1930s) underground discharge from the Rock Island Coal Company #7 mine near the town of Hartshorne, Pittsburg County, Oklahoma (Fig. 1). Prior to construction, the mine discharge was sampled periodically for several years and showed considerable fluctuation in both water quality and quantity. Measured discharge rates ranged from <1 to approximately 75 LPM. Metal and anion concentrations varied with each sampling event, although temperature, pH, and DO remained relatively consistent (Table 1). The acidic nature of the discharge, coupled with median concentrations of Fe and Mn of 765 and 18mg/L, respectively, warranted a plan for treatment.

An abandoned fan shaft (total depth approximately 56 m) from which the water discharged in an artesian manner was converted to the VALD and serves as the first process unit in the passive treatment system (Fig. 1). The VALD was designed to perform similarly to a traditional horizontally-oriented ALD. The shaft was first filled with approximately 34 m of local dolomitic stone (to provide long-term stability) which was then covered by 22 m of high calcite limestone (to provide alkalinity generation capacity). An effluent header pipe directs water from the VALD to the remainder of the passive treatment system, consisting of an alternating series of three oxidation ponds and two vertical flow cells, before discharging to a polishing wetland cell and then into an existing pond (Behum et al., 2004; Behum and Kim, 2004). Because this study

focuses solely on alkalinity generation in the VALD, performance of the remaining process units is not discussed.

Table 1. Summary data for untreated mine discharge near Hartshorne, OK from 1999 to 2002.

	Minimum	Maximum	Median	n
Temperature (°C)	17.4	22.3	20.9	18
pH	5.25	5.64	5.36	18
DO (mg/L)	0.1	0.8	0.2	17
Specific conductance (µS/cm)	2960	17100	11800	18
Alkalinity (mg/L)	95	214	117	18
Acidity (mg/L)	419	2402	1405	15
Iron (mg/L)	215	1311	765	15
Manganese (mg/L)	14	29	18	15
Sodium (mg/L)	1400	3437	1893	4
Calcium (mg/L)	259	380	320	9
Magnesium (mg/L)	170	361	230	8
Chloride (mg/L)	197	381	225	9
Sulfate (mg/L)	5456	13620	7842	12

We evaluated the VALD monthly since water began flowing in January 2007 after a prolonged regional drought. Temperature, pH, DO, oxidation-reduction potential, total dissolved solids, conductivity, and specific conductance were determined *in situ* with a YSI 600QS multiparameter datasonde and YSI 650MDS display. Total alkalinity and turbidity were measured immediately after sample collection via titration with appropriate normality H₂SO₄ using a Hach digital titrator (Method 8203) and via a Hach 2100P Turbidimeter, respectively. Volumetric discharge rates were determined with a calibrated bucket and stopwatch. Samples were collected in 250-mL HDPE bottles for each sample location-event pair. One sample was preserved with trace metal grade HNO₃ to pH <1 for total metal analyses and a second sample was stored on ice at ≤4°C for anion analyses. Samples were then transported to the Center for Restoration of Ecosystems and Watersheds (CREW) laboratories at the University of Oklahoma for analyses.

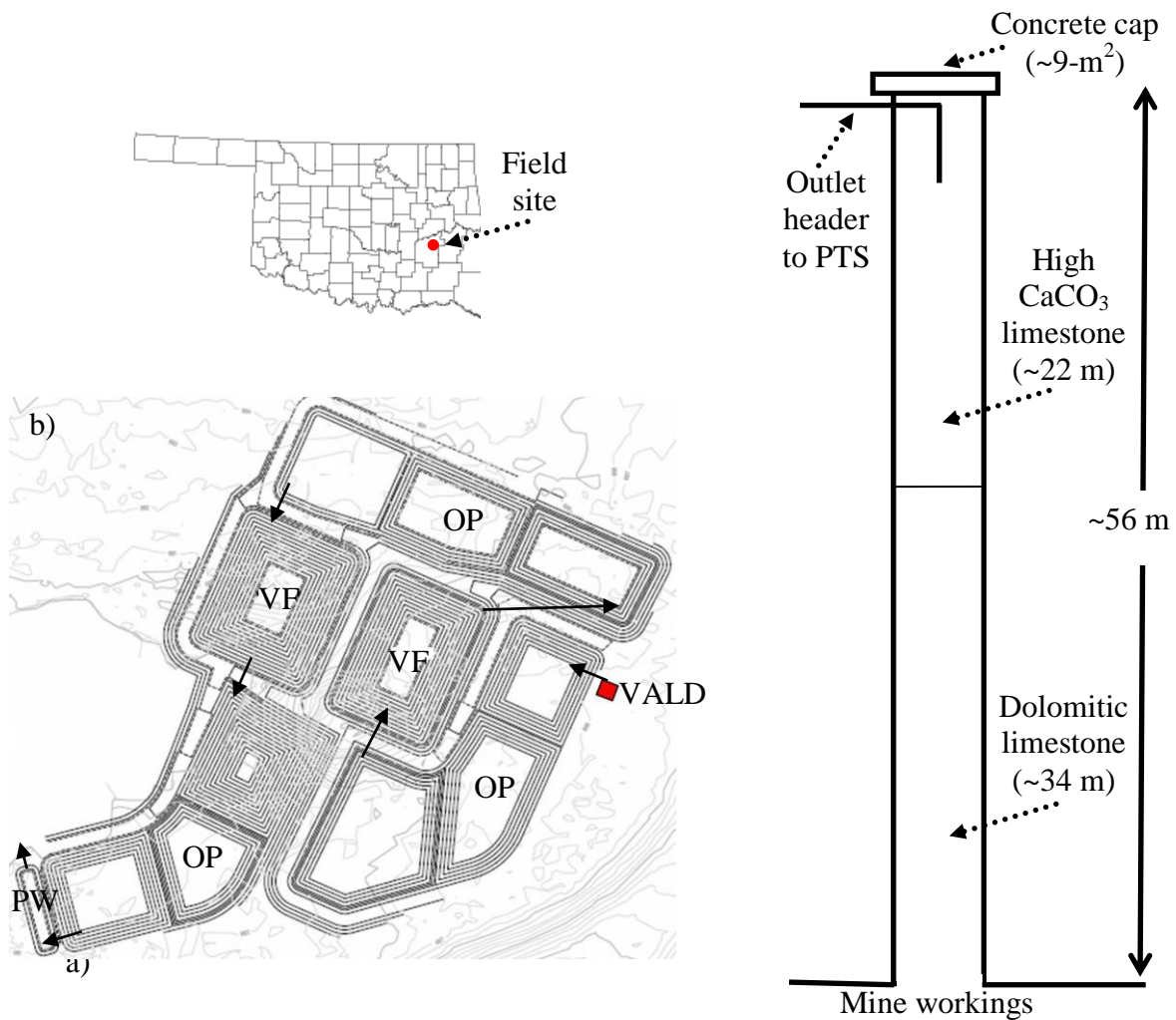


Figure 1. Rock Island #7 field site showing a) location within Oklahoma, b) schematic of passive treatment system with location of VALD (base drawing courtesy Burns and McDonnell, 2004) showing general direction of flow; OP = oxidation pond; VF = vertical flow cell; PW = polishing wetland, and c) generalized diagram of VALD (after Behum et al., 2004; note: *not to scale*)

Preserved samples for metals analyses were first HNO₃ digested in a CEM MARSXpress Digestion System following EPA Method 3015 (EPA, 2006). Digested samples were then analyzed with a Varian Vista-PRO simultaneous axial Inductively Coupled Plasma-Optical Emission Spectrometer following EPA Method 6010 (EPA, 2006) for 15 analytes (Al, As, Ca, Cd, Co, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Zn). Samples retained for anion analysis were filtered through 0.2µm nitrocellulose filters and analyzed with a Dionex 300 ion chromatograph

following EPA Method 300.0 (EPA, 1993) for seven analytes (Br⁻, Cl⁻, F⁻, NO₂⁻, NO₃⁻, PO₄³⁻, SO₄²⁻).

Results and Discussion

Water quality and quantity data collected from the VALD effluent since January 2007 demonstrate that these waters are highly mineralized, containing elevated metals, base cations, SO₄²⁻ and Cl⁻. The wide range of values is consistent with pre-construction data. These data also show considerable variability over the sampling period (Table 2), as expected, given the established inconsistency in source water quality and quantity. However, temperature, pH, and DO remained relatively consistent over the sampling period. Maximum values for all metals, all anions, alkalinity and conductivity occurred in the first sampling event after the VALD first began to flow. Alkalinity concentrations averaged 474 ± 52 mg/L during the period of study.

Table 2. Summary data from VALD discharge for data collected January to October 2007.

	Minimum	Maximum	Median	n
Temperature (°C)	20.1	21.0	20.6	11
pH	6.06	6.21	6.14	11
DO (mg/L)	0.4	2.2	0.8	11
Specific conductance (µS/cm)	5366	13517	7987	11
Alkalinity (mg/L)	407	556	453	11
Acidity (mg/L)	541	2231	1241	11
Iron (mg/L)	298	1227	681	11
Manganese (mg/L)	4.3	18.9	11.3	11
Sodium (mg/L)	772	2791	1527	11
Calcium (mg/L)	509	632	568	11
Magnesium (mg/L)	151	437	267	11
Chloride (mg/L)	118	292	164	8
Sulfate (mg/L)	3340	8984	6154	8
TDS (g/L)	3.8	9.7	5.5	11
Discharge rate (LPM)	29	63	44	7

Detention Time

Alkalinity concentrations in the VALD effluent were not significantly related to calculated detention times ($r^2 = 0.03$; $p=0.82$). Detention times ranged from 25 to 53 hours for this period of study with mean and standard deviation of 37 ± 9 hours. Previous studies (e.g., Watzlaf et al., 2004) identified a necessary nominal retention time of approximately 15 hours to reach maximum alkalinity generation in ALDs. Furthermore, maximum sustained alkalinity concentrations are reported to be no more than approximately 300 mg/L. Although much longer detention times and greater alkalinity concentrations were found for the VALD, no statistical relationships were identified given the limitations of the initial data set. Initial alkalinity data were the result of an unknown prolonged detention time for at least part of the VALD. As monitoring continues at this site, detention time effects on alkalinity generation will be further examined.

CO₂ Partial Pressure

Mine pool P_{CO_2} was evaluated as a factor contributing to elevated concentrations of alkalinity produced by the VALD. Calculated P_{CO_2} was found to be particularly elevated in the VALD discharge, ranging from $10^{-0.22}$ to $10^{-0.51}$ atm. As shown in Fig. 2, alkalinity, through the increased solubility of calcite, was significantly related to P_{CO_2} ($r^2=0.61$, $p=0.003$). Despite this relationship between alkalinity and P_{CO_2} , measured alkalinity concentrations were substantially lower than calculated alkalinity concentrations based upon equilibrium data from Watzlaf et al. (2004). In any case, elevated P_{CO_2} does appear to play a substantial role in alkalinity generation in the VALD.

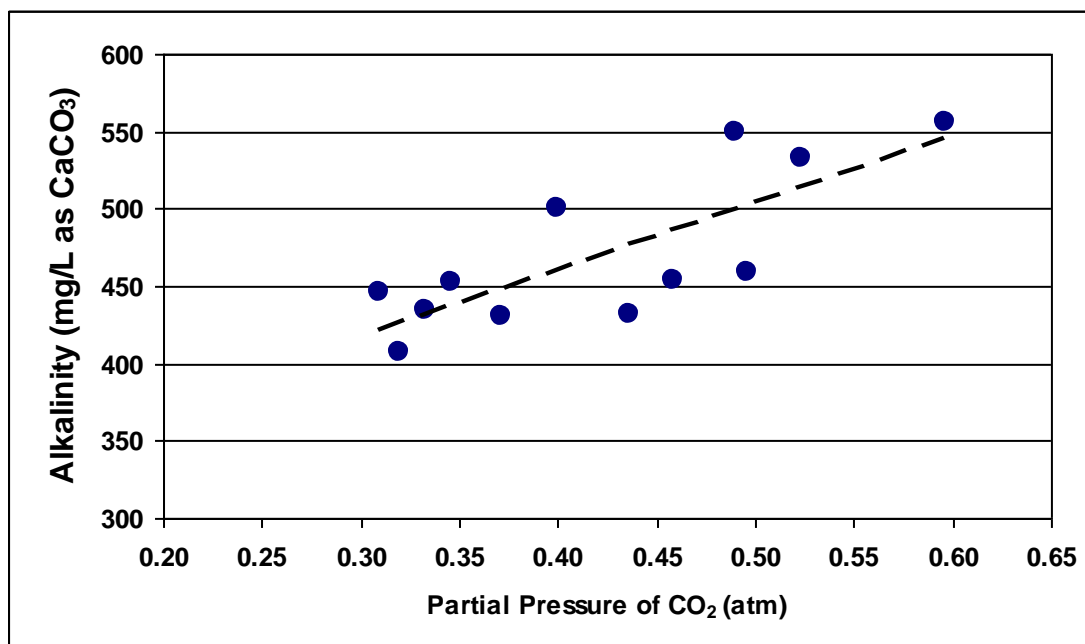


Figure 2. Measured alkalinity as a function of calculated P_{CO_2} in the VALD discharge showing best fit linear regression line with $r^2 = 0.61$.

Ionic Strength

The impact of ionic strength on the solubility of calcite was also considered as a possible explanation for the elevated alkalinity concentrations found at the VALD discharge. The Langelier Approximation (Equation 3) was used to calculate the ionic strength of the VALD discharge.

$$I = \text{TDS (mg/L)} \times 2.5 \times 10^{-5} \quad (3)$$

This equation uses total dissolved solids (TDS) concentration to approximate the ionic strength (Yen, 2007). TDS concentrations were obtained *in situ* at each sampling event via multiparameter datasonde along with the other water quality parameters.

Based on the results of this calculation, ionic strength varied from a maximum of 0.24 at the first sampling event to a minimum of 0.09 later in the year. Pure water is considered to have an ionic strength of 0, while the average ionic strength of seawater is ~ 0.7 . The ionic strength of the VALD discharge was, on average, considerably higher than pure water with a median value of 0.15 ± 0.05 . These results were compared to the alkalinity concentrations measured during each of the sampling events and a strong significant relationship ($r^2=0.89$, $p=4 \times 10^{-6}$) was found (Fig. 3).

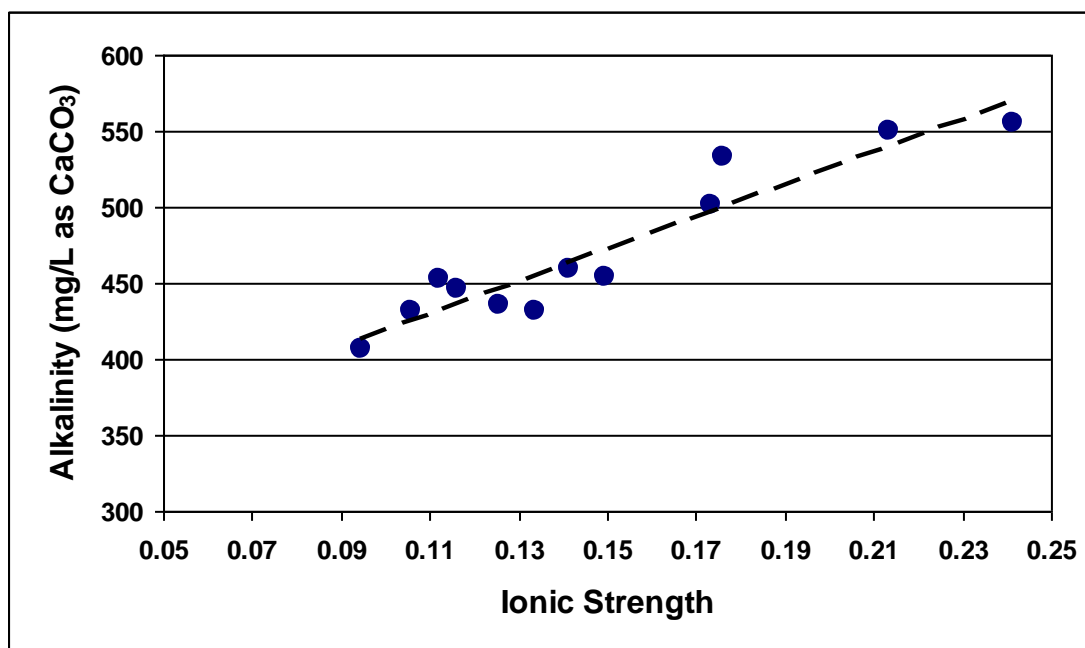


Figure 3. Measured alkalinity as a function of calculated ionic strength in the VALD discharge showing best fit linear regression line with $r^2 = 0.89$.

Although this particular mine drainage contains elevated concentrations of several typical mine drainage ions (e.g., Fe, Mn, Ca, and Mg), Na and SO_4^{2-} concentrations were particularly elevated in comparison to typical mine drainage. In a survey of 156 coal mine drainages, Watzlaf et al (2004) reported maximum concentrations of 712mg/L Na and 1100mg/L SO_4^{2-} . Median and maximum values in these mine waters were 1527 and 2791 mg/L for Na and 6154 and 8984 mg/L for SO_4^{2-} , respectively; far exceeding the typical concentrations expected. These two constituents were likely the most significant contributors to total ionic strength of the water. Sodium and SO_4^{2-} were each compared to ionic strength (Fig. 4). Both Na ($r^2 = 0.95$, $p=4.5 \times 10^{-7}$) and sulfate ($r^2=0.97$, $p=5.7 \times 10^{-6}$) demonstrated strong positive and statistically significant relationships with ionic strength.

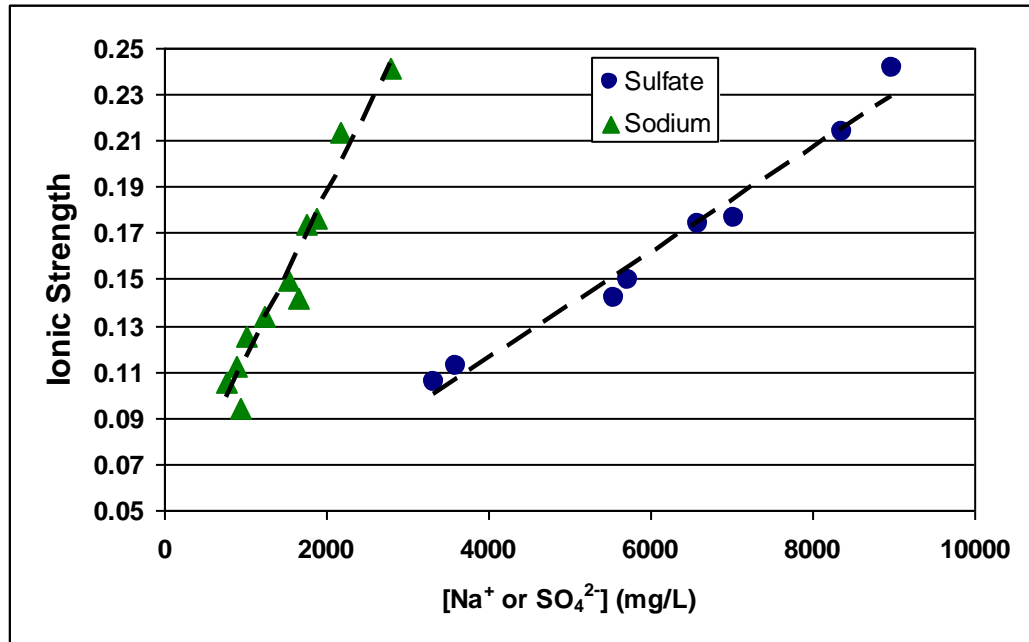


Figure 4. Calculated ionic strength as a function of Na and SO₄²⁻ concentrations showing best fit linear regression lines with $r^2 = 0.95$ for Na and 0.97 for SO₄²⁻.

Multiple Regression Model

For the portion of the data set where complete flow rate information was available, a multiple regression model was developed in an attempt to further understand alkalinity generation in the VALD. For this portion of the data set, the identified influences of detention time, P_{CO_2} , and ionic strength individually explained 7%, 56% and 80% of the variability in the effluent alkalinity concentrations, created by the dissolution of calcite. However, when all three factors are included in a multiple regression analysis, 97% of the variability is accounted for at $p=0.02$ (Equation 4 and Fig. 5).

$$\text{Alkalinity} = 87.1(P_{CO_2}) + 1457(I) + 2.17(t_d) + 149 \quad (4)$$

Removal of the detention time term decreases the fit significantly ($r^2=0.90$, $p=0.04$) and therefore this term was included in the analysis.

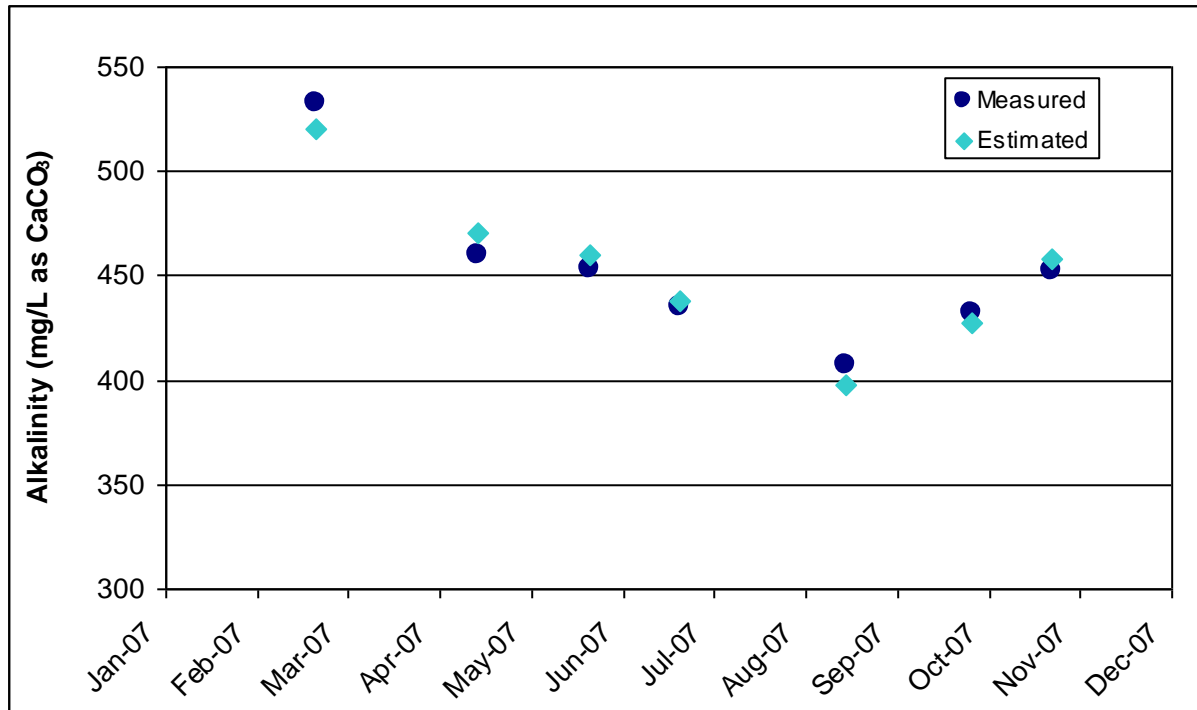


Figure 5. Measured and regression-estimated alkalinity as a function of time for the VALD discharge.

Conclusions

It appears that a combination of adequate detention time, elevated P_{CO_2} , and naturally-high ionic strength influence alkalinity generation in the VALD, at least during the first year of operation. Although detention times were 2.3 to 3.5 times the recommended minimum design detention time of 15 hours little relationship existed between detention time alone and alkalinity generation in the VALD. Calculated P_{CO_2} concentrations did appear to significantly influence calcite dissolution and therefore effluent alkalinity concentrations, although not at the expected levels based on equilibrium conditions. Ionic strength was a principal determining factor for effluent alkalinity concentrations, through the increased solubility of calcite, and was elevated beyond levels found in typical mine drainages. The impact of Na and SO_4^{2-} concentrations on ionic strength of the mine discharge is quite evident and may point to a possible method for enhancement of alkalinity generation in ALDs. The combination of VALD alkalinity generation, coupled with metal retention in traditional aerobic ponds and wetlands and further alkalinity generation in vertical flow cells, produces markedly improved water quality in this system.

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