Carbonation of mine water to increase calcite dissolution

Robert Hedin and Benjamin Hedin

Hedin Environmental, 195 Castle Shannon Blvd, Pittsburgh PA USA
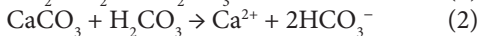
Abstract

Experiments were conducted on the ability of mine water carbonation to increase alkalinity generation by limestone aggregate in a closed environment. Carbonation increased the amount of alkalinity obtainable from limestone and increased the kinetics of alkalinity generation. The most effective results were obtained from a membrane carbonator and AASHTO 8 limestone aggregate where 3.8 kg of CO2 increased alkalinity generation by 1.0 kg (as CaCO3). The findings have applications for mine waters with high concentrations of divalent metals and acidities that exceed the capabilities of standard limestone-based passive technologies.

Keywords: Carbonation, calcite dissolution, passive treatment, acid mine drainage

Introduction

Limestone (calcite) is the most common acid-neutralizing and alkalinity-generating material used in passive mine water treatment systems. Calcite's solubility and dissolution kinetics can limit its utility in passive systems, especially for mine waters containing high concentrations of Fe(II) and Mn(II). Dissolved carbon dioxide is an important controller of calcite dissolution in natural and mine water treatment systems. The hydrolysis of dissolved CO2 produces carbonic acid (reaction 1) which reacts with calcite to produce dissolved calcium and bicarbonate (reaction 2).

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (1)$$
$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \qquad (2)$$
$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O \qquad (3)$$

Bicarbonate, which is considered alkalinity in mine water applications, neutralizes acidity and buffers pH between 6 and 8 (reaction 3). The circumneutral alkaline conditions created by calcite dissolution are especially suitable for the oxidation and precipitation of Fe(II) and Mn(II).

Mine water commonly contain high concentrations of CO_2 due to the in-mine neutralization of acid produced by pyrite oxidation. Natural waters in equilibrium with atmospheric conditions contain approximately $10^{-3.5}$ atm CO_2 and when

placed in contact with calcite yield 40-60 mg/L alkalinity (as CaCO3). Coal mine drainages in the eastern United States commonly contain $10^{-2.5}$–$10^{-1.5}$ atm CO_2 and when placed in contact with calcite yield 150−350 mg/L alkalinity. This capacity of many mine waters to produce high concentrations of alkalinity when placed in contact with calcite in a closed environment is the chemical basis for the anoxic limestone drain technology and also a contributor to the effectiveness of bioreactor technologies.

The amount of bicarbonate alkalinity produced naturally from calcite is limited by solubility considerations. This limitation becomes important in the treatment of waters with high concentrations of Fe(II) and Mn(II) because the acidity produced through the oxidation and hydrolysis of these metals can exceed the alkalinity produced from calcite dissolution. The passive aerobic treatment of these insufficiently buffered waters typically results in effluents with residual Fe and Mn and pH < 6. In northwestern PA there are dozens of coal mine discharges that contain more than 100 mg/L Fe(II), dozens of mg/L Mn(II), and more than 250 mg/L mineral acidity. Due to calcite solubility limitations, the treatment of these discharges in anoxic limestone drains yields only partial neutralization of the acidity. Treatment of the water to circumneutral pH with low Fe and Al requires additional alkalinity generation. The conventional methods for

adding more alkalinity to these waters are the addition of either a vertical flow pond (e.g., SAPS, Kepler and McCleary 1994) or a final oxic limestone bed.

In conventional passive treatment planning, the chemical conditions of the influent are considered fixed and the system design is focused on selection and sizing of technologies appropriate for those conditions. Pre-treatment modification of the chemistry is not commonly considered. This paper describes a project where CO_2 was added to mine water that was subsequently reacted with limestone in a closed environment.

Methods

All experiments were conducted at the Orcutt Smail site, a closed underground coal mine in Jefferson County, Pennsylvania (PA). Acidic mine drainage is currently treated with a lime slurry addition, aeration, and settling in ponds.

Mine water was carbonated before exposure to high calcite limestone (hereafter referred to as "limestone") in a closed environment. CO_2 was obtained from commercial suppliers of gas for the food and welding industries. Both pressurized gas in cylinders and liquid CO_2 in dewars were used. CO_2 was introduced using conventional aeration nozzles and membrane technology. CO_2 addition occurred in the influent mine water feed, referred to as "in-line" carbonation, and within the limestone bed, referred to as "in-bed" carbonation. The limestone beds were experimental units constructed in steel open-top tanks (roll-off boxes). The tanks were filled with limestone aggregate and plumbed to provide horizontal flow. The first round of experiments were conducted with AASHTO 5 aggregate which has an average diameter of 19 mm and calculated surface area of 1.44 cm²/g (Cravotta 2021). The second round of experiments were conducted with AASHTO 8 aggregate which has an average diameter of 7 mm and calculated surface area of 4.44 cm²/g. Anoxic conditions were assured in the tanks with a 15 cm cap of compost or plastic taped to the sides of the tank. Water levels in the tanks were maintained at the top of the limestone aggregate by adjusting the effluent pipe.

Water samples were collected from the influent and effluent of the limestone bed. Flow rates were measured at the effluent with a bucket and stopwatch. The porosity of the beds was calculated from the flooded volume, an aggregate density of 1.61 tonne/m³, and an aggregate porosity of 42%. Theoretical retention times (TRT) were calculated by dividing the porosity of the bed by the flow rate. Field measurements were made *in situ* of pH, temperature, and conductivity using a calibrated Hanna combination pH meter. Alkalinity was measured within 15 minutes of sample collection via titration with 1.6 N sulfuric acid to pH 4.5 using a Hach digital titrator and bromocresol indicator. Samples were collected for laboratory analysis of major cations, anions, and acidity (APHA 1999). Metals (cations) were measured on a sample acidified in the field with nitric acid to pH < 3. Separate samples were collected for direct measurement of CO_2 using a commercial beverage carbonation meter (Vespar and Edenborn 2012). The samples were collected in plastic soda bottles, capped and sealed to prevent outgassing of CO_2, and measured at the Vespar laboratory at West Virginia University.

CO_2 was also estimated for samples with known pH and alkalinity values from equation 4.

$$CO_2 + H^+ * HCO_3^- / 10^{-9.12} \qquad (4)$$
Where CO_2, H^+, and HCO_3^- are mole/L.
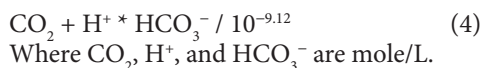
Alkalinity generation was calculated from the difference of influent and effluent alkalinity concentrations converted to loads using the effluent flow rates. CO_2 consumption was determined from the difference of influent and effluent CO_2 measurements/calculations and from gas flow meters installed between the CO_2 injection and limestone bed influent.

Results and Discussion

Table 1 shows the average chemistry of the influent mine water. This water is similar to many net acidic discharges in the region that have pH 5–6 and high concentrations of Fe and Mn.

Table 1. Average influent to experimental units

pH	Alk	Acid	Fe	Mn	Al	Ca	Mg	K	Na	SO$_4$	Zn	Co	Ni
	mg/L CaCO$_3$		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L
5.7	103	147	103	40	<1	151	106	5	2	914	710	509	575

Initial experiments were conducted with 25 m³ roll-off containers filled with ASSHTO 5 limestone (90% calcite) and capped with compost to assure maintenance of anoxic conditions. Without carbonation and with TRT of 8–12 h, the beds discharged water with average 243 mg/L alkalinity. Nozzle carbonation increased effluent alkalinity to as much as 475 mg/L (Fig. 1). Effluent alkalinity was directly related to carbonation between 100 and 1500 mg/L CO_2 addition. Two experiments conducted at higher carbonation rates did not result in increased alkalinity generation.

Experiments were conducted using in-line and in-bed carbonation methods. Differences between the methods were minor and not statistically significant (Fig. 1).

Fig. 2 shows alkalinity generation by the experimental units when the TRT was varied. In the absence of carbonation, the maximum alkalinity of approximately 250 mg/L required 11–12 h of contact time. When the beds were carbonated with about 300 mg/L CO_2, and effluent containing 250 mg/L was produced

with only 3–4 h of TRT. This result indicates that modest carbonation can markedly decrease the sizing of limestone beds.

A second series of experiments were conducted using an in-line membrane carbonator and smaller ASSHTO 8 limestone aggregate. The experimental unit was a 9 m3 rectangular roll-off tank that was sealed with plastic. The membrane carbonator was typical of ones used to carbonate liquids in beverage bottling operations. Operation of the membrane carbonator required pressurized gas and water conditions. Gas pressure was provided by pressured CO_2 cylinders. Water pressure was provided by an electric pump. Membrane carbonation experiments were conducted at TRTs of 1–2 h. Fig. 3 shows the results of membrane carbonation experiments overlain on the results of the nozzle carbonation experiments. Membrane carbonation produced significantly more alkalinity than nozzle carbonation. At higher carbonation levels the membrane produced 70% more alkalinity per unit of CO_2 added than the nozzle method.
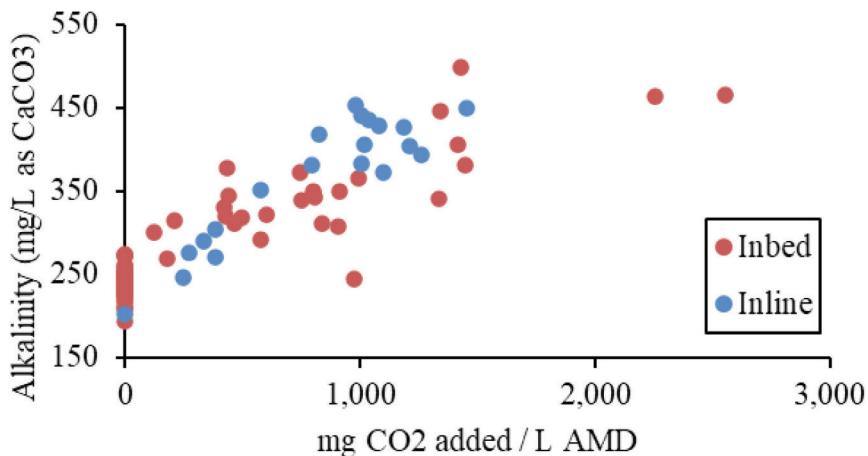

Figure 1 The relationships between CO_2 added and effluent alkalinity concentrations from the pilot-scale roll off containers at the Orcutt site. The relationships between CO2 added and effluent alkalinity concentrations was similar between in-bed and in-line CO_2 addition technologies
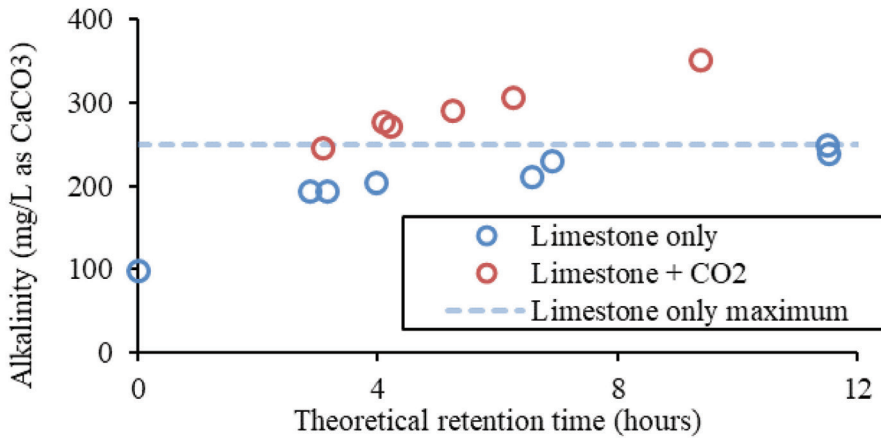
Figure 2 *Theoretical retention time in pilot-scale experiments with corresponding effluent alkalinity concentrations with and without CO_2 additions. CO_2 was added via in-line technologies in the experiments shown here. CO_2 additions were 246 – 575 mg/L and averaged 364 mg/L*

Fig. 3 underestimates the benefits of membrane carbonation because the membrane experiments were conducted at a TRT of 1–2 h while the shortest TRT times used for the nozzle experiments were 3-4 h (Fig. 2). The three nozzle experiments, conducted at 3.1–4.2 h TRT, produced extra alkalinity at a rate of 0.06 mg/L alkalinity per mg/L CO_2 added per hour. The membrane carbonator produced extra alkalinity at a rate of 0.19 mg/L extra alkalinity per mg/L CO_2 added per hour. The results show that that more efficient transfer of CO_2 combined with smaller limestone aggregate results in the higher rates of alkalinity generation.

Process cost evaluations indicate the CO_2 is the primary driver of cost for the carbonation/limestone system. The
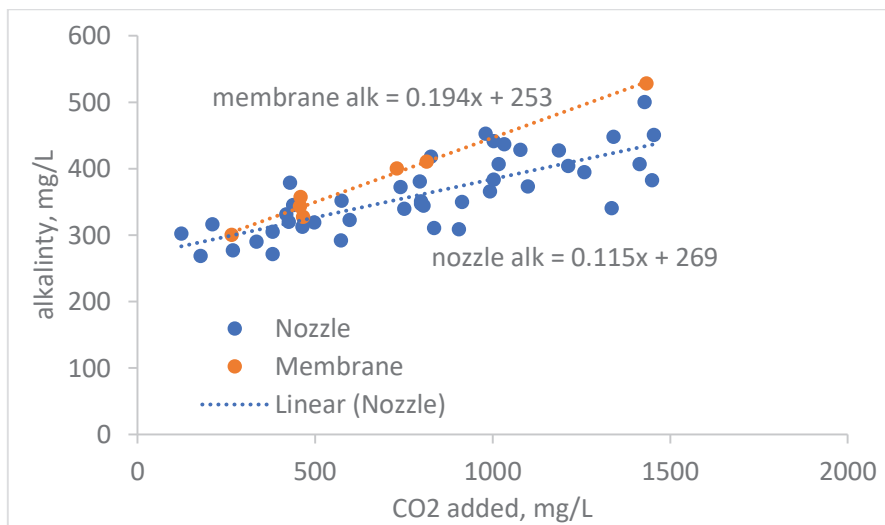

Figure 3 *Relationship between CO_2 additions (mg/L) and effluent alkalinity (mg/L). The blue values indicate carbonation with a nozzle. The orange values indicate carbonation with a membrane unit*

economic feasibility of the technology will be largely driven by the efficiency of CO_2 utilization. CO_2 usage efficiency was measured by calculating the ratio of CO_2 addition to alkalinity generation. During the first phase of experiments using nozzle carbonation and AASHTO 5 aggregate, the CO_2:Alk ratio averaged 7.4 (s.d. 2.9, n = 34), indicating that 7.4 kg of CO_2 was needed to produce 1.0 kg of extra alkalinity. Table 2 shows efficiency calculations for the membrane carbonator and AASHTO 8 experiments. The average CO_2:Alk ratio was 3.8 (s.d. 0.5, n = 6) which indicates a doubling of the CO2 utilization efficiency.

Conclusions

Alkalinity generation by limestone aggregate was increased through carbonation of the mine water. Limestone treatment of AMD at the test site typically produces 250 mg/L alkalinity with 10−12 h of TRT. Carbonation resulted in 250 mg/L alkalinity after 3 h TRT and effluent alkalinity concentrations as high as 528 mg/L. The most effective result was obtained with a membrane carbonator and ASSHTO 8 limestone aggregate which produced, on average, 1 kg extra alkalinity per 3.7 kg of CO_2 addition.

Acknowledgements

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Table 2. Experimental results using the membrane carbonator and AASHTO 8 limestone

TRT	CO_2 input	Alk out	CO_2 used	Extra Alk	CO2:Alk
min	mg/L	mg/L	kg/hr	kg/hr	ratio
100	0	218	0.0	0.0	na
63	460	357	1.49	0.45	3.3
100	457	343	0.93	0.21	3.7
105	343	528	2.80	0.61	4.6
100	1434	400	1.49	0.37	4.0
100	731	411	1.67	0.39	4.2
100	266	300	0.54	0.17	3.2