

# The complicated role of CO<sub>2</sub> in mine water treatment

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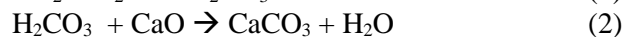
## Abstract

Elevated concentrations of CO<sub>2</sub> are common in discharges from abandoned coal mines. CO<sub>2</sub> is a problem in lime treatment systems because of its tendency to react with lime and precipitate as calcite. In passive systems elevated CO<sub>2</sub> can maintain pH values between 5.5 and 6.5, which is low enough to substantially slow Fe and Mn oxidation reactions. The typical solution for elevated CO<sub>2</sub> is degassing through aeration which lessens the formation of calcite in lime systems and raises pH in passive systems. However, CO<sub>2</sub> can also provide benefits in treatment systems. Most passive treatment systems generate alkalinity through limestone dissolution. CO<sub>2</sub> enhances the dissolution and results in higher concentrations of alkalinity. This study evaluated the effect of CO<sub>2</sub> on limestone dissolution by measuring alkalinity generation of limestone that received fresh mine water with high CO<sub>2</sub> and stale mine water with low CO<sub>2</sub>. Fresh mine water generated twice the alkalinity as stale mine water. The results demonstrate that the effect of CO<sub>2</sub> on a treatment system's performance varies with the technology being utilized.

Key words: mine water treatment, limestone, carbon dioxide

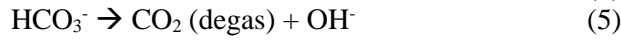
## Introduction

Metal and sulfate contaminated mine waters discharging from coal mines or spoil piles commonly contain elevated concentrations of CO<sub>2</sub> (Hedin et al. 1994a; Jarvis 2006). As the mine water flows through a treatment stream the CO<sub>2</sub> can degas to the atmosphere, precipitate into a solid, or discharge in the liquid effluent as carbonic acid (H<sub>2</sub>CO<sub>3</sub>), bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) or carbonate ion (CO<sub>3</sub><sup>2-</sup>). In lime treatment systems where the dissolution of CaO or Ca(OH)<sub>2</sub> creates high concentration of Ca<sup>2+</sup> and high pH, the formation and precipitation of calcite, CaCO<sub>3</sub>, is favored.

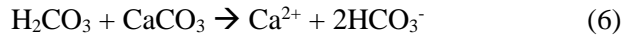


The formation of CaCO<sub>3</sub> results in treatment inefficiencies because neutralization is transferred to the solid sludge, not to the mine water. In the coal fields of northern Appalachia, many lime treatment plants operate inefficiently due to the formation of CaCO<sub>3</sub>. Means et al (2016) analyzed the treatment efficiency of four systems that treated high-CO<sub>2</sub> Fe-contaminated mine water with lime. Calcite formation consumed 29-58% of the alkaline addition in the systems. A recent study of the chemical composition of solids produced by mine water treatment plants in Pennsylvania found that eight lime sludges averaged 54% CaCO<sub>3</sub> (TU 2016).

CO<sub>2</sub> is an important factor in passive treatment systems. Alkaline mine waters with high CO<sub>2</sub> have high concentrations of carbonic acid (reaction 1) which generally buffers between 5.5 and 6.5. This pH range is low enough to slow oxidation rates for Fe<sup>2+</sup> and Mn<sup>2+</sup> to impractical levels. The degassing of CO<sub>2</sub> through passive means or mechanical aeration increases pH (reaction 5) which can significantly increase rates of Fe and Mn removal (Hedin et al. 1994b)



These examples of the benefits provided by decreasing CO<sub>2</sub> suggest that degassing should be a primary interest in systems dealing with high CO<sub>2</sub>. However, there are circumstances where CO<sub>2</sub> is advantageous to treatment. The dissolution of limestone, the most commonly used alkaline reagent in passive systems, is enhanced by CO<sub>2</sub>.



The significance of reaction 6 in passive systems has not been quantified so it is difficult to estimate the impact of CO<sub>2</sub> degassing on the treatment performance of a passive system.

In this paper the effect of CO<sub>2</sub> management in limestone-based treatment systems is measured through limestone incubation experiments. In the two mine waters tested, the degassing of CO<sub>2</sub> from mine water prior to contact with limestone is found to decrease the alkalinity-generating capacity by 40-50%. The results illustrate the complexity of CO<sub>2</sub> management between types of treatment systems and even between treatment units within the same system.

## Methods

Alkalinity generation potential was measured with a device referred to as an *Alkast* (alkalinity forecaster). The device consists of a 140 ml plastic syringe, a mesh bag of sieved, washed, and weighed material that fits inside the syringe, and an airtight cap (Figure 1). The mesh bag fills approximately ½ of the syringe volume. This allows the plunger to be moved so that water can be drawn into and dispelled from the device. Once the device is filled with water, the plunger is pushed so that it is flush with the syringe contents, and the syringe tip is capped. The device is then incubated for a set period of time. The incubation ends when the water contents are flushed out using the plunger. After its use the *Alkast* device is rinsed with tap water and is ready to be used in another test.

In these experiments, the *Alkasts* were filled with 120 grams of sieved (2-4 mm) washed calcitic (90% CaCO<sub>3</sub>) limestone. The water samples produced were filtered (0.22 μm) and measurements were made of pH, temperature, and conductivity with a calibrated Hanna HI 991300 meter. Alkalinity was measured by titration with 1.6 N H<sub>2</sub>SO<sub>4</sub> to pH 4.5. Alkalinity and acidity are expressed as mg/L CaCO<sub>3</sub>.

Two treatments of mine water were considered in the experiments. Fresh mine water was collected from its source with minimal exposure to the atmosphere. When testing fresh mine water *Alkast* devices were filled with water withdrawn from the discharge zone or water collected from the discharge zone and maintained in a closed container until use in experiments. Stale mine water was collected at a point downstream of the discharge after it had been aerated or was generated by allowing fresh mine water to equilibrate with the atmosphere over a minimum 2-day period.

Samples of the influent and effluent of limestone treatment systems were collected and analyzed in the field for pH, temperature, alkalinity, and conductivity and by a laboratory for acidity, Fe, Mn, Al, and sulfate using standard analytical procedures.



**Figure 1** The standard composition of an Alkast is a 140 mL syringe, a mesh bag with material, and an airtight cap.

### Study Sites

The Woodlands passive treatment system is located at the Pittsburgh Botanic Garden, Pennsylvania, USA, and has been operating since April 2013. The system includes a 409 mton open limestone bed followed by a polishing pond and flush pond. The system treats acid water containing Al (Table 1). This project focused on the influent and effluent of the limestone bed. The influent to the bed is a buried pipe that connects to an underground coalmine. Water flows directly from the mine into the bed without aeration and is considered fresh mine water. The limestone bed was installed open to the atmosphere, however the Botanic Garden has since constructed a walking trail on top of it by covering it with geotextile and fine aggregate and the bed operates as a closed system.

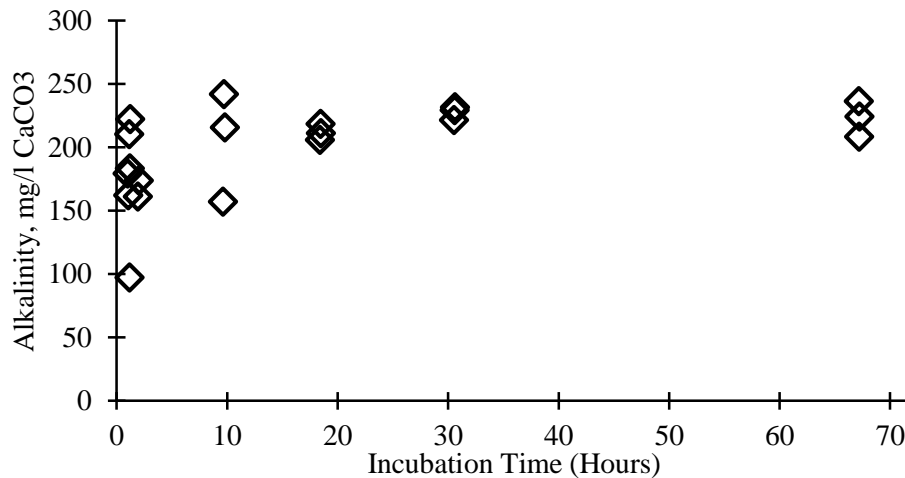
The Fall Brook South and North passive treatment systems are located near Blossburg, Pennsylvania, USA and have both been operating since November 2015. The South system contains 9,091 mton of calcitic limestone in three parallel limestone beds followed by two ponds. The North system contains 1,680 mtons of calcitic limestone in a single limestone bed followed by one pond. The limestone beds receive acid water from a common abandoned underground coal mine, but the chemistry varies somewhat (Table 1). The mine water (MW) at the North system is collected underground and transferred to the system with minimal aeration. Water samples were collected for *Alkast* testing at the system influent. Because of landowner issues, the MW at the South system could not be collected at its source. Instead it flows approximately 50 m down a steep rocky channel before it is collected into a pipe that delivers the water to the limestone beds. Water samples were collected for *Alkast* testing at the discharge point (fresh) and at the collection pipe influent after aeration (stale).

**Table 1** Influent characteristics of Woodlands, Fall Brook South, and Fall Brook North treatment system

	flow L/min	pH	Alk mg/L	Acid mg/L	Fe mg/L	Al mg/L	Mn mg/L	SO4 mg/L
Woodlands	30	3.2	0	143	0.6	16.3	0.8	474
Fall Brook South	3,125	3.5	0	89	0.6	10.6	13.2	360
Fall Brook North	512	3.5	0	67	2.7	11.5	9.4	213

## Results

Figure 1 shows *Alkast* alkalinity concentrations for the Woodlands influent at varying incubation periods. Over short incubation periods of 1-2 hours the *Alkast* results were variable. Beyond ten hours the alkalinity concentrations stabilized at similar values and averaged 221 mg/L. The DLB during this period had a theoretical retention time of approximately 40 hours and discharged water with 197 mg/L alkalinity.



**Figure 2** Alkalinity concentrations for *Alkast*s containing fresh Woodlands MW at different incubations periods. The limestone at this time discharged 197 mg/L alkalinity

Table 2 shows alkalinity measurements for the treatment system effluents and the *Alkast* testing on a variety of mine waters collected at the sites. The Fall Brook South system was sampled under average and high flow conditions (15 and 5 hour retention times, respectively). Variation in alkalinity generated by *Alkast* incubation of the system effluent was similar to variation in the alkalinity generated by the limestone beds (compare “System effluent” and “*Alkast*, system effluent”). The *Alkast* method overestimated alkalinity generation by the limestone beds by 12% at the Woodlands site and 25% at the Fall Brook sites. The cause of the overestimation is suspected to be related to limestone particle size (much smaller in the *Alkast*s) and the loss of CO<sub>2</sub> in the mine water between its sampling point and its entry into the limestone beds.

The Woodlands and Fall Brook North system receive a fresh influent while the Fall Brook South system receives an aerated stale influent. When the Woodlands mine water was allowed to equilibrate with the atmosphere, the *Alkast* alkalinity for the stale water was 40% lower than the fresh water. When the Fall Brook South MW was collected at its source, the *Alkast* alkalinity for this fresh water was 80-110% higher than was obtained for the stale system effluent.

**Table 2** Concentrations of alkalinity for samples collected at the Woodlands (Wood), Fall Brook South (FBS), and Fall Brook North (FBN) passive limestone treatment systems.

	Wood	FBS	FBS	FBN
System influent water type	Fresh	Stale	Stale	Fresh
System theoretical retention, hr	36	15	5	14
System effluent, alkalinity mg/L	197	78	61	125
<i>Alkast</i> , system influent, alkalinity mg/L	221	97	76	158
<i>Alkast</i> , system effluent, alkalinity mg/L	na	97	89	147
<i>Alkast</i> , fresh influent, alkalinity mg/L	---	206	162	---
<i>Alkast</i> , stale influent, alkalinity mg/L	128	---	---	na

When pH is measured on *Alkast* effluents, the CO<sub>2</sub> partial pressure can be calculated from the pH, alkalinity, and carbonate equilibria constants. The Woodlands fresh and stale waters had CO<sub>2</sub> partial pressure of 10<sup>-1.70</sup> and 10<sup>-2.32</sup>, respectively. For context, water in equilibria with the atmosphere has a CO<sub>2</sub> partial pressure of 10<sup>-3.5</sup>.

### Discussion

Calcite formation is a costly side reaction in lime treatment that can be avoided in chemical treatment systems by switching to a non-Ca reagent or by removing CO<sub>2</sub>. Means et al (2016), working only with net alkaline discharges, found that switching to hydrogen peroxide eliminated calcite formation and decreased treatment costs substantially. For acid waters that require the addition of alkaline reagent, the removal of CO<sub>2</sub> via aeration prior to lime addition is a recommended practice. The recently constructed Hollywood treatment system in Elk County Pennsylvania treats a low-pH acidic mine water with lime. The mine water is vigorously aerated prior to lime addition and the sludge produced is only 10% CaCO<sub>3</sub>. Two nearby lime plants that treat similar water but without aeration generate sludge that is 40-70% CaCO<sub>3</sub>. Calcite formation in lime plants without CO<sub>2</sub> management decreases useful alkalinity generation by 50-100% with major cost impacts.

In passive systems, the impact of the CO<sub>2</sub> on alkalinity generation is opposite what is observed in lime systems. Where limestone is utilized as the alkaline reagent, CO<sub>2</sub> enhances dissolution of the limestone and increases the generation of useful alkalinity. In the limestone incubation tests fresh mine water with elevated CO<sub>2</sub> produced water with 93-109 mg/L higher alkalinity than tests conducted with stale water with decreased CO<sub>2</sub>. Many passive systems that treat acid mine water discharge to streams degraded by untreated mine water from abandoned mines. In these cases, treatment systems should generate as much alkalinity as possible. The simplest method for ensuring the maximum amount of alkalinity is to prevent any degassing of CO<sub>2</sub> prior to treatment with limestone.

In some cases, maximum alkalinity generation is not a priority and the generation of excessive alkalinity may be viewed as wasteful. In these cases, the current solution is to decrease the quantity of limestone and thus lessen contact time. This approach is problematic when flows increase or when the limestone dissolves, both of which could decrease the retention time below a critical minimum. The results here suggest an alternative method where alkalinity generation is controlled through CO<sub>2</sub> management.

CO<sub>2</sub> management strategies can vary within a treatment system. As noted earlier, CO<sub>2</sub> can buffer pH less than 6.5 which impacts Fe and Mn removal. Degassing increases pH. A common situation in Pennsylvania coal fields is acid water with Fe concentrations greater than 100 mg/L where passive treatment consists of limestone pretreatment followed by oxidation and settling

ponds. In this case, CO<sub>2</sub> should be maintained as high as possible in the limestone treatment units and decreased as low as possible in the oxidation ponds.

### **Conclusions**

Mine waters commonly contain elevated concentrations of CO<sub>2</sub>. The handling of CO<sub>2</sub> should differ depending on the treatment technology. In lime treatment systems, where CO<sub>2</sub> promotes treatment inefficiency due to calcite formation, CO<sub>2</sub> should be removed. In limestone treatment systems, where CO<sub>2</sub> promotes alkalinity generation, CO<sub>2</sub> should be conserved.

The *Alkast* methodology presented here provides a simple procedure for experimentally measuring the effect of mine water handling on limestone dissolution. In experiments on mine water from two sites, the *Alkast* testing indicated that CO<sub>2</sub> degassing decreased the alkalinity generation capacity of limestone treatment by 80-100 mg/L.

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