Increased Generation of Alkalinity from Limestone through Carbonation
Hedin Environmental
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Concept

The treatment of acidic mine water requires the addition of alkalinity. Conventional sources of alkalinity are lime (CaO) and caustic (NaOH) which are costly. Limestone is a much less expensive alkaline reagent but its use in mine water treatment systems is restricted because of solubility and kinetic limitations. Limestone dissolution is highly dependent on dissolved carbon dioxide concentrations. Hedin Environmental recently completed an EPA SBIR Phase I project that investigated alkalinity generation by a combined limestone ($CaCO_3$) and carbon dioxide (CO_2) system ("$CaCO_3$+CO_2"). The six-month project confirmed that alkalinity generation by limestone could be enhanced and accelerated through carbonation. Cost analyses indicate that optimized technology, combined with bulk pricing for industrial CO_2, can generate alkalinity at a cost substantially less than caustic and competitive with lime.

2020 Project

An EPA SBIR Phase I project supported the installation and operation of two experimental limestone reactors (photo). Untreated mine water containing 150 mg/L acidity (as $CaCO_3$), 100 mg/L Fe^{2+}, and 40 mg/L Mn^{2+} was fed into the units at adjustable flow rates. CO_2 was injected into the influent water before interaction with limestone or within the flooded limestone bed. Experiments were conducted that varied mine water flow rate, mode of CO_2 injection, and CO_2 flow rate. Alkalinity generation was measured through field and laboratory measurements of water samples collected at influent and effluent stations.

Pilot-scale limestone-filled containers used for $CaCO_3$+CO_2 experiments.

Experiments confirmed the ability of the $CaCO_3$+CO_2 technology to increase alkalinity generation compared to limestone alone. The increased generation of alkalinity was directly related to CO_2 addition (Figure 1). Retention time studies indicated that CO_2 addition also increased the rate of alkalinity generation. An alkalinity concentration that required 10-12 hours to achieve without CO_2 was achieved in 3 hours with carbonation (Figure 2).

Next Steps

The next tasks for development of the $CaCO_3$+CO_2 technology development include: 1) optimization of the technology for use in mine waters with high concentrations of Fe^{2+} and Mn^{2+}, and 2) expanding the applicability of the technology to acid mine waters containing Al^{3+} and Fe^{3+}. Both tasks can be implemented at coal mine sites in western Pennsylvania. The $CaCO_3$+CO_2 technology is also appropriate for mine drainage from metal mines and a pilot system is under consideration for a metal mine site in the western US. The application of the technology to mine waters contaminated with Al^{3+} and Fe^{3+} and to metal mines will substantially expand its potential utilization.

Commercialization

Three potential adopters of the $CaCO_3$+CO_2 technology have been identified. First, existing underperforming passive treatment systems could be retrofitted to increase performance. This is a specialized market limited at this time to a few dozen systems in the eastern US. The more significant application is as an alternative to conventional lime and caustic technologies. Existing chemical treatment systems could be retrofitted to accommodate the $CaCO_3$+CO_2 technology. There are hundreds of potential system modifications at mining sites around the world. Finally, the most impactful use of the technology will be as part of new acid mine drainage treatment systems. Dozens of chemical treatment systems are installed annually at abandoned and active mine sites around the world. The designers of these systems will be receptive to alternative cost-effective technology.

A New CO_2 Market

Adoption of the $CaCO_3$+CO_2 technology will create a new market for industrial grade CO_2. Current analyses suggest that the $CaCO_3$+CO_2 technology will consume 0.5-1.0 ton/yr CO_2 per gallon per minute (gpm) of flow. In mining districts with acid mine drainage tendencies, the generation of 5,000-10,000 gpm of total flow is not uncommon. The potential demand for CO_2 in one of these districts would be several thousand tons CO_2 per annually. There are dozens of mining districts in the US and hundreds around the world.

Lower Greenhouse Gas Emissions

The $CaCO_3$+CO_2 technology could play an important role in efforts to decrease emissions of CO_2, a potent greenhouse gas. The $CaCO_3$+CO_2 technology has a significantly smaller greenhouse gas footprint than conventional lime technologies because it avoids the calcination process needed to produce lime. Additionally, the CO_2 utilized in the systems will be primarily sourced from industrial operations that would have, otherwise, released the CO_2 to the atmosphere.

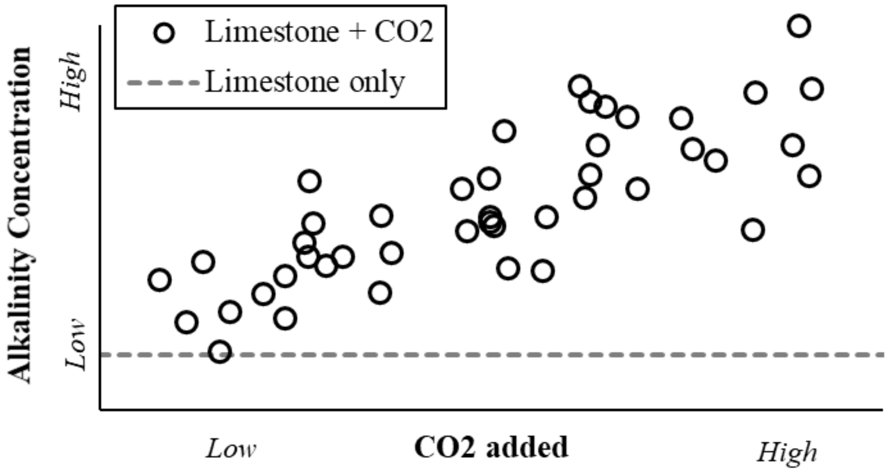

Figure 1. Relationship between CO_2 addition and alkalinity generation by the pilot scale limestone system constructed for the EPA SBIR Phase I project. The maximum alkalinity concentration achieved from limestone alone is shown for reference.

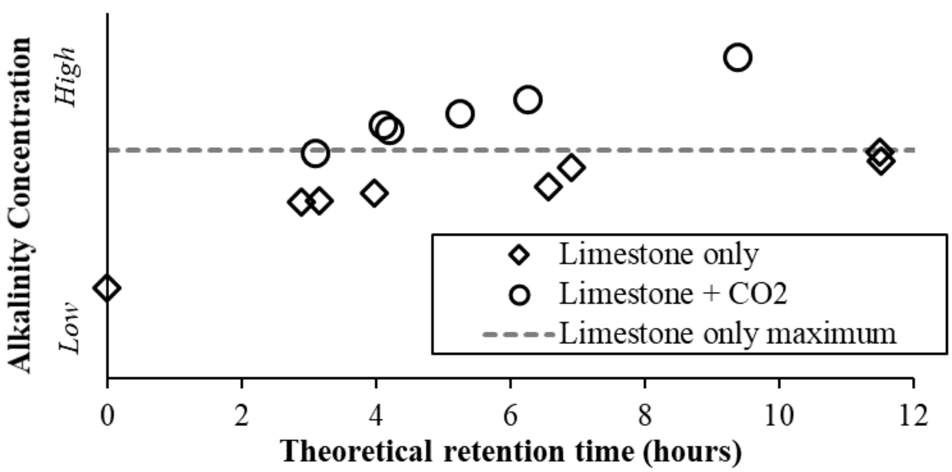

Figure 2. Effect of carbonation on the rate of alkalinity generation from limestone.