Carbon Dioxide Pretreatment of AMD for Limestone Diversion Wells

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ABSTRACT

Neutralizing acidity and increasing alkalinity of water degraded by acid mine drainage (AMD) is typically achieved through direct addition of base materials, including anhydrous ammonia, calcium hydroxide, and limestone. Limestone is desirable given its relatively low cost and reduced hazard potential associated with handling or application. Limestone use is restricted, however, by slow dissolution rates and problems associated with development of a metal hydroxide coating on the limestone particles. We describe equipment designed to circumvent these problems through the use of pulsed bed technology and carbonation pretreatment. In operation, a timer-relay valve assembly directs water intermittently into a bed of small particle size (1 mm) limestone, to expand the bed and allow for bed turnover and contraction. During bed expansion, water is introduced at twice the normal rate providing high particle attrition and turbulence. Water flow is interrupted prior to particle carryover in the effluent. Altering the extent of the settling period provides for control of retention time/treatment effect, which is needed when AMD composition and flow varies seasonally. Transfer of carbon dioxide into the AMD prior to treatment increases the rate of limestone dissolution through temporary development of high free carbon dioxide concentrations and increased acidity. High concentrations of free carbon dioxide encourage dissolution of limestone via the reaction:

$CaCO_3 + H_2O + CO_2$ «$Ca^{2+} + 2HCO_3^-$

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

The carbon dioxide pretreatment accelerates gas absorption by exposing the AMD to carbon dioxide enriched gas at elevated pressures (100 psi). Carbon dioxide saturation concentrations can be increased by a factor of 22,000. The equipment under development allows carbon dioxide not utilized in the first pass through the system to be captured and re-used to minimize make-up gas requirements and maximize effluent pH. Laboratory tests have established the capability of the equipment to accelerate limestone dissolution rates well

beyond rates achieved with alternate designs and to provide effluent alkalinities in excess of 1,000 mg/L as $CaCO_3$. The ability to supertreat AMD allows for sidestream treatment, reducing significantly the size of the reactor and required plumbing as well as costs associated with alternate pretreatment steps, e.g. removal of debris, dissolved oxygen, and dissolved metals.

BACKGROUND/RESOURCE NEED

Acid mine drainage (AMD) significantly degrades surface waters in the coal deposit regions of Appalachia and the Ohio River basin. Direct effects of acidification on fish include acute mortality, reproductive failure, altered growth rates and chronic impairments to body organs and tissues. Negative indirect effects of acidification include fish habitat degradation and increases in concentrations of soluble toxic metals, such as aluminum. In Pennsylvania alone AMD had degraded 2,600 miles of streams resulting in an annual loss of revenues associated with sport fishing of 67 million dollars.

Mitigation of AMD is typically achieved through direct addition of alkaline materials, followed by clarification. High costs limit widespread application of treatment. With currently available technology, it has been estimated that 5 billion dollars will be required to correct AMD related problems in Pennsylvania. Alkaline materials used to neutralize mine acid include anhydrous ammonia, sodium hydroxide, sodium carbonate, calcium hydroxide, calcium oxide, and limestone. Use of limestone is desirable given its relatively low cost and widespread availability. Moreover, limestone is less caustic than alternative reagents, thus, use of limestone reduces the hazards of handling and application. Limestone dissolution also provides calcium ions needed to reduce the toxicity of certain dissolved metals. Unfortunately, limestone use is restricted due to the slow dissolution (acid neutralizing) rates and problems associated with the development of a metal hydroxide coating of the limestone particles.

AGENCY/CLIENT NEEDS

1. Congressman William Clinger requested that the Wellsboro staff pursue research needed to develop and evaluate cost effective treatment methods for AMD. His request was based on the severe impact of AMD in his district, unique research capabilities at the Wellsboro Laboratory in the area of conservation technology, and the close proximity of the laboratory to AMD impacted streams.
2. The NBS recently signed the "Statement of Mutual Intent for the Restoration and Protection of Streams and Watersheds Polluted by Acid Mine Drainage from Abandoned Coal Mines" put forth by EPA and Office of Surface Mining (OSM). Signing parties agreed to work to increase the understanding and applications of the best technology available for remediating and preventing mine drainage, and to support the development of new technologies.
3. Private and state conservation groups as well as the coal mining industry recognize the need for new cost effective AMD treatment methods.

STATE-OF-KNOWLEDGE

Several types of equipment have been used to dose AMD with limestone, including the diversion well, a technology developed in Scandinavia and recently applied with relatively low initial capital and maintenance costs at several Pennsylvania AMD sites. The diversion well is designed to establish a fluidized bed of crushed limestone 6 - 25 min in diameter. Fluidization occurs within a cylindrical well that receives water through a centrally located down pipe discharging water at the bottom of the well. The diverted water flows upward through the limestone with sufficient force to agitate and fluidize the media causing abrasion of the aggregate for enhanced dissolution. The treated water then escapes over the lip of the well or through an outlet pipe. Diversion wells tested in Pennsylvania are typically 2 in in diameter, 3 in deep, and half filled with 20 min limestone. Hydraulic head required for operation is about 3 in. Head is developed by constructing a dam up stream and laying large diameter pipe between the dam and the diversion well. Although this technology provides low total costs of treatment, treatment effect is severely limited by the short hydraulic retention times required for fluidization, and by the use of relatively large aggregate diameters.

OBJECTIVES

Improve the treatment efficiency, reduce operating costs and broaden the flow handling capability of limestone diversion well (fluidized bed) reactors.

RESEARCH APPROACH

The rate of limestone dissolution is related to particle size, composition, turbulence, temperature, water chemistry, and the presence or absence of metal hydroxides or precipitates that tend to coat the stone. The rate of limestone ($CaCO_3$) dissolution is accelerated when inlet water acidity (H^+) is high e.g.

$CaCO_3 + H^+$ « $Ca^{+2} + HCO_3^-$ (1)

$$CaCO_3 + H^+ \rightleftharpoons Ca^{+2} + HCO_3^-, \quad (1)$$

and when aggregate size is small. Reducing aggregate size within a conventional diversion well reduces significantly the flow required for fluidization, a factor that limits hydraulic loading rates. We circumvent these undesirable effects by utilizing pulsed-bed technology, recently developed at Wellsboro. In operation, a valve assembly intermittently directs water into a small particle size (1 mm) bed of limestone, so as to expand the bed and allow for bed turnover and contraction (Figure 1). During bed expansion, water is introduced at twice the normal rate providing for high levels of particle attrition and turbulence. Water flow is interrupted prior to loss of particles in the effluent. Altering the extent of the settling period allows for control of retention time/treatment effect. Control of this type is needed when AMD composition and flow varies seasonally.

Following equation (1), as the acidity of AMD is reduced by exposure to limestone within a reactor, the rate of acid neutralization slows rapidly making it difficult to achieve needed changes in water chemistry (pH, acidity, alkalinity). The equipment under development at Wellsboro is designed to avoid this problem by incorporating a unique carbonation pretreatment step. Here the transfer of carbon dioxide into the AMD prior to treatment increases the rate of limestone dissolution through temporary development of high free carbon dioxide concentrations and increased acidity (lowers pH). The high free carbon dioxide concentrations encourage the dissolution of limestone via the reaction given below.

$CaCO_3 + H_2O + CO_2$ « $Ca^{+2} + 2HCO_3^-$ (2)

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca^{+2} + 2HCO_3^- \quad (2)$$

Drawing on earlier research at Wellsboro in the area of gas transfer, the carbon dioxide pretreatment step has been designed to accelerate gas absorption by exposing the AMD to carbon dioxide enriched gas at elevated operating pressures (100 psi). Carbon dioxide saturation concentrations can be increased by a factor of 22,000. Following treatment in the limestone bed, the equipment under development allows for capture and reuse of carbon dioxide not utilized in the first pass through the system (Figure 1), so as to minimize make-up gas requirements and maximize effluent pH. Lab scale tests are planned to establish a correlation among the following design variables: hydraulic loading, bed depth, particle size, retention time, carbon dioxide concentrations, and treatment effect. This data will then be used to establish desirable operational parameters for a field scale system capable of handling a low of 250 - 500 gpm. This system will be constructed at Wellsboro and subjected to a 4-month continuous operation test prior to movement into an appropriate AMD field site. Treatment effects, operating costs, and maintenance requirements, along with the response of aquatic insects and fish downstream of the treatment unit, will then be established over a 2 year operating period. Concurrent laboratory studies will address fish physiology and behavioral research needs of the project.

TEST METHODS

We constructed a treatment unit prototype capable of handling AMD flow rates of 15 L/min. Figure 2 shows the major components of the system - - four 10 cm diameter pressure vessels charged with granular limestone, a centrifugal pump, a packed tower carbonator, and a timer-relay control system used to direct the systems 3-way electric ball valves. In operation, two of the four limestone beds (columns 1 and 2) receive recycle water alternately from the carbonator, under pressure, to maintain high free carbon dioxide concentrations and to accelerate limestone dissolution. Pressure is provided by carbon dioxide entering the carbonator from a Dewar type storage tank. System pressure is set by tank regulator pressure. Following treatment (4 min), both columns are isolated from the carbonator by the control system, then vented to the atmosphere allowing degassing to occur as the treated water is displaced from the columns by incoming AMD. Concurrently, columns 3 and 4 are coupled with the carbonator, pressurized, and alternately expanded by recycle pump flow. This switch over occurs every four minutes and a constant discharge from the treatment unit is maintained (Figure 3).

We evaluated system performance using all combinations of the following design variables: influent acidity, 9, 200, 555 and 1025 mg/l as $CaCO_3$; system operating pressure, 0, 10, 30, 60 and 100 psig. Each unique set of operating conditions was replicated once providing a total of 40 observations. We also operated the system using two different treatment cycles (4 min, 8 min) at each of three operating pressures (0, 30 and 100 psig) and two influent acidities (9 mg/L and 1000 mg/L). In all tests AMD was simulated by adding sulfuric acid to well water with the following characteristics: pH, 6.7; acidity, 9 mg/L; alkalinity, 30 mg/L; water temperature, 9 - 10^{0}C. Performance was assessed by measuring changes in these variables across the system during treatment both with and without air stripping of dissolved carbon dioxide. Acidity and alkalinity were measured by titration using standard methods (American Public Health Association). The pH was measured electrochemically. Least squares regression analysis was used to establish correlations among performance variables and operating conditions.

RESULTS

Laboratory tests demonstrated the ability of the new equipment to accelerate limestone dissolution well beyond rates established with alternative equipment designs. Carbon dioxide pressure and influent acidity effects on effluent alkalinity and the mass of limestone dissolved per liter treated are shown in Figures 4 thru 7. The response of both variables to increases in regulator pressure (Figure 4 and 6) were fit with the model

$$Y = a + b X^{0.5} \qquad (3)$$

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Coefficients of determination (r^2) were high ranging between 0.980 to 0.997. The mass of limestone dissolved per liter increased directly with influent acidity (Figure 5) at each regulator pressure tested following the general model

$$Y = a + b X \qquad (4)$$

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Here r^2 ranged between 0.986 and 0.999. Influent acidity did not influence effluent alkalinity (Figure 7) with positive regulator pressures. Figure 8 shows water pH levels in excess of 8 can be achieved with air stripping of free CO_2, and Figure 9 shows that doubling the treatment cycle length has little effect on the mass of limestone dissolved per liter treated with high influent acidities.

SUMMARY

A pulsed bed limestone-water contactor was developed that accelerates limestone dissolution rates through use of a carbon dioxide pretreatment step. Mineral acidities in excess of 1000 mg/L were neutralized and unusually high levels of alkalinity were achieved during treatment. The ability of the equipment to super-treat the AMD, should in many cases, allow for sidestream treatment (Figure 10). Side streaming eliminates the need to dam the entire flow and reduces significantly the size of the reactor and plumbing required for treatment; in other words it reduces capital and site preparation costs. Further, given that water flow through the treatment unit can represent a fraction of total flow, costs associated with removal of trash, leaf litter, dissolved oxygen and dissolved metals are minimized.

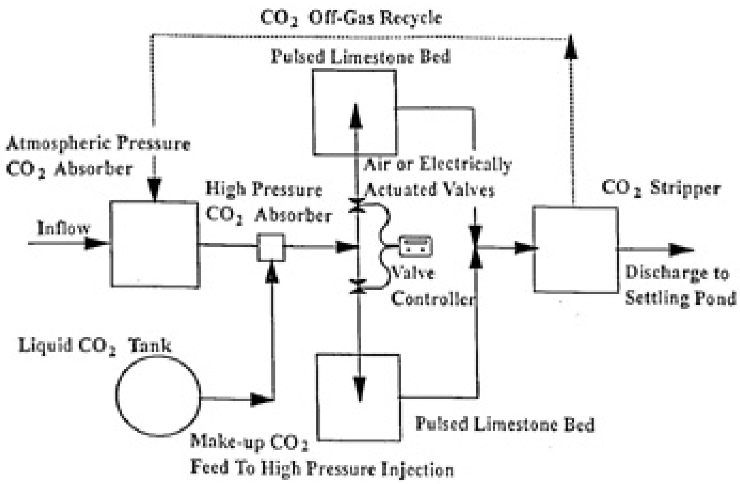

Figure 1. Schematic of flows through a pulsed bed system incorporating carbon dioxide pretreatment for enhanced restoration of acid mine drainage.

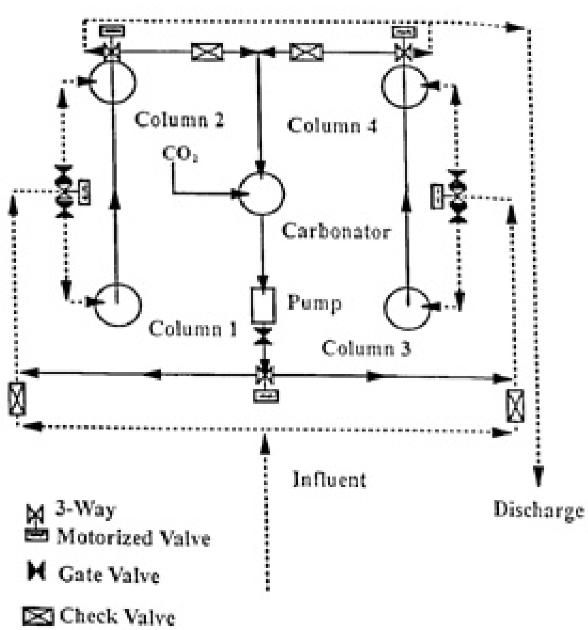

Figure 2. Major components of the test limestone dissolution system.

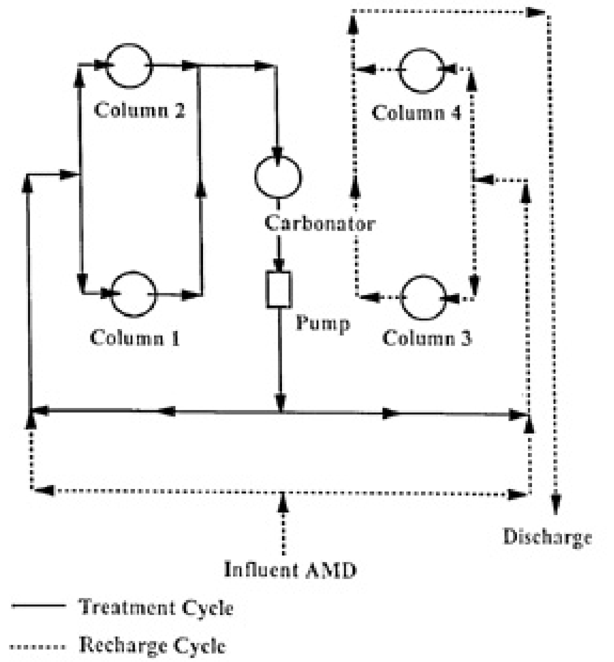

Figure 3. Treatment and recharge cycle flows through the limestone dissolution system.

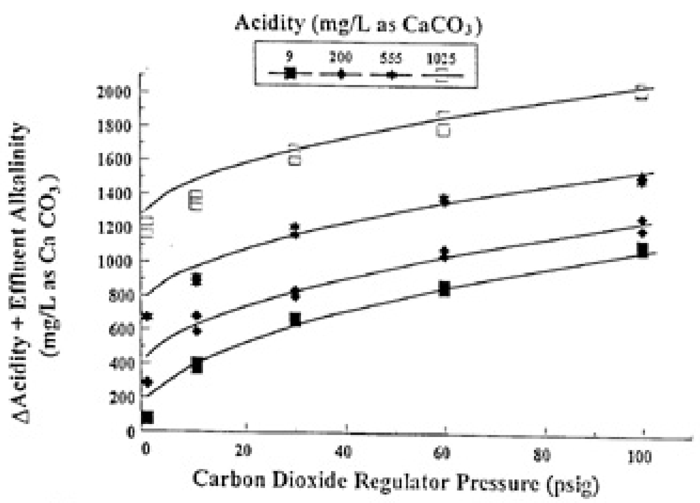

Figure 4. Effect of carbon dioxide regulator pressure on the mass of limestone dissolved (Δacidity + effluent alkalinity) during treatment of water representing four levels of acidity.

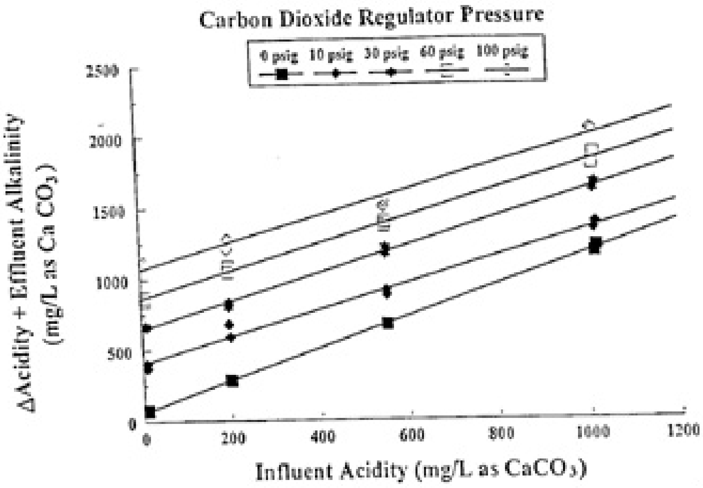

Figure 5. Effect of inlet acidity on the mass of limestone dissolved (Δacidity + effluent alkalinity) when operating at five different regulator pressures.

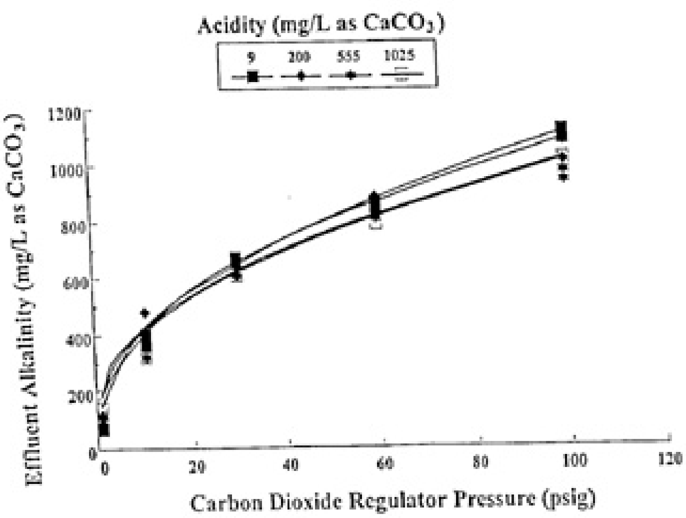

Figure 6. Effect of carbon dioxide regulator pressure on effluent alkalinity during treatment of waters representing four levels of acidity.

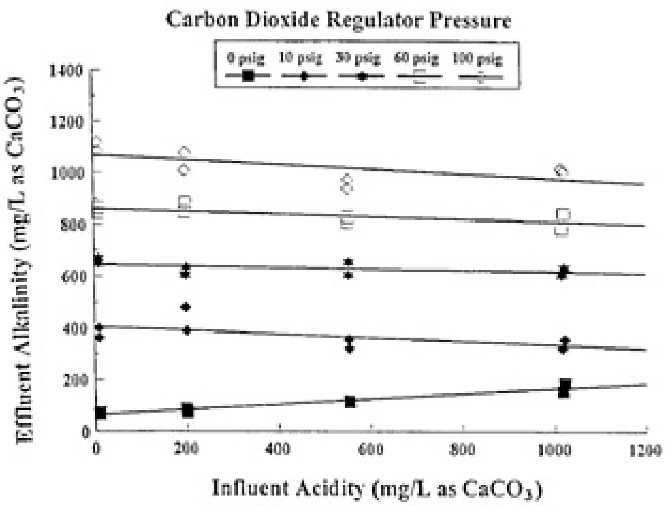

Figure 7. Effect of influent acidity on effluent alkalinity when operating at five different regulator pressures.

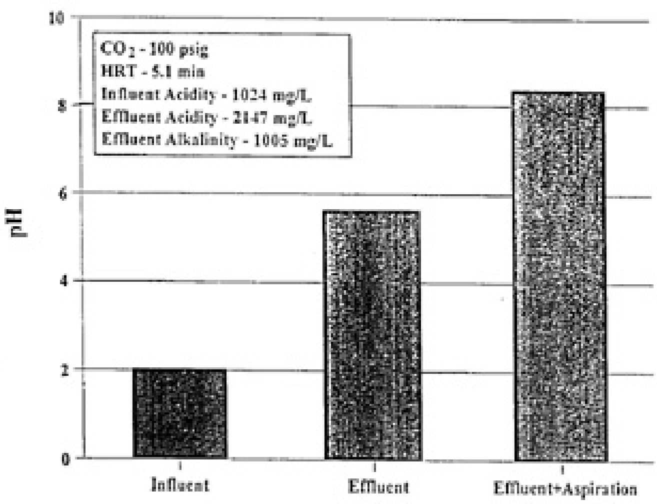

Figure 8. Test water pH before and after treatment.

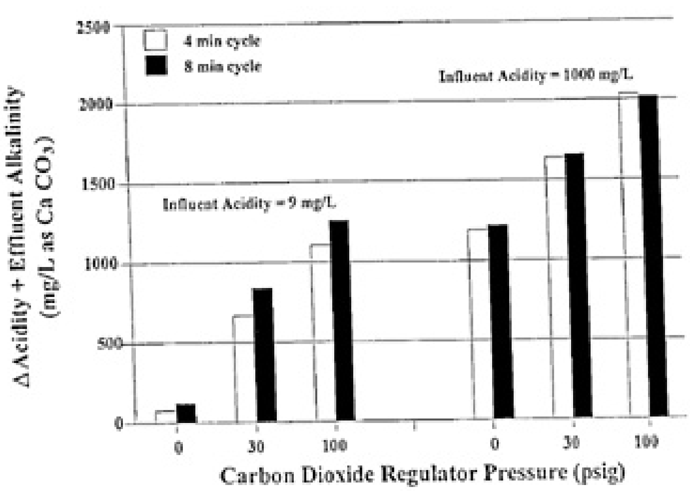

Figure 9. Effect of treatment cycle duration on the mass of limestone dissolved (Δ acidity + effluent alkalinity) when operating at three different regulator pressures and two inlet acidities.

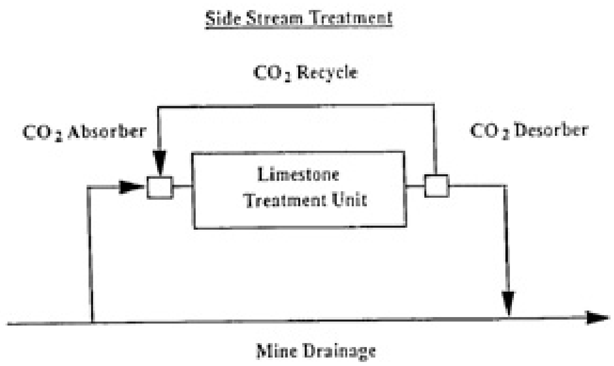

Figure 10. Schematic of flows with side stream treatment.