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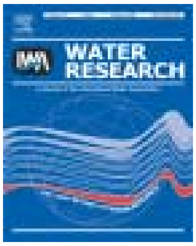

# Effect of temperature, hydraulic residence time and elevated $P_{CO_2}$ on acid neutralization within a pulsed limestone bed reactor

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## abstract

Limestone has potential for reducing reagent costs and sludge volume associated with treatment of acid mine drainage, but its use is restricted by slow dissolution rates and the deposition of Fe, Al and Mn-based hydrolysis products on reactive surfaces. We evaluated a pulsed limestone bed (PLB) reactor (15 L/min capacity) that uses a $CO_2$ pretreatment step to accelerate dissolution and hydraulic shearing forces provided by intermittent fluidization to abrade and carry away surface scales. We established the effects of hydraulic residence time (HRT, 5.1–15.9 min), temperature (T, 12–22 °C) and $CO_2$ tension ($P_{CO_2}$, 34.5–206.8 kPa) on effluent quality when inlet acidity (Acy) was fixed at 440 mg/L ($pH = 2.48$) with $H_2SO_4$. The PLB reactor neutralized all $H^+$ acidity ($N = 80$) while concurrently providing unusually high levels of effluent alkalinity (247–1028 mg/L as $CaCO_3$) that allow for side-stream treatment with blending. Alkalinity (Alk) yields rose with increases in $P_{CO_2}$, HRT and settled bed height (BH, cm) and decreased with T following the relationship ($R^2 = 0.926$; $p < 0.001$): $(\mathrm{Alk})_{\text{non-filtered}} = -548.726 + 33.571 \cdot (P_{CO_2})^{0.5} + 33.671 \cdot (\mathrm{HRT}) + 7.734 \cdot (\mathrm{BH}) - 5.197 \cdot (\mathrm{T})$. Numerical modeling showed $CO_2$ feed requirements for a target Alk yield decrease with increases in HRT, T and the efficiency of off-gas ($CO_2$) recycling.

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## 1. Introduction

Mining processes resulting in acid deposition have had a significant negative effect on aquatic resources in many parts of the world, including the loss of important fisheries (Maree et al., 1996; Starnes and Gasper, 1995; Cole et al., 2001a, b). Acid mine drainage (AMD) results primarily from the dissolution of the metallic sulfide $FeS_2$, and its subsequent oxidation to sulfuric acid (Evangelou, 1995). This reaction is followed by the hydrolysis of the product $Fe^{3+}$ to the insoluble product ferric hydroxide ($Fe(OH)_3$). Acid generated here and in the first oxidation step forces the solubilization of certain base metals, including $Al^{3+}$ and $Mn^{2+}$, that contribute acidity as well as additional solids while undergoing alternate hydrolysis reactions (Evangelou, 1995; Hedin et al., 1994). Treatment of AMD requires the addition of an alkaline reagent followed by gravity separation of the insoluble reaction products such as Fe and Al hydroxides. Limestone ($CaCO_3$) has potential for reducing reagent costs (Hedin et al., 1994), sludge volume (Dempsey and Jeon, 2001; Sibrell and Watten, 2003) and risk of over treatment (Olem, 1991) but its use has been restricted by a sensitivity to armoring by certain scale forming reactions that inhibit transport of $H^+$ and its products at the solid–liquid interface (Lovell, 1973; Ziemkie-

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wicz et al., 1997). Scales of particular concern include Fe, Al and Mn oxides as well as gypsum ($CaSO_4 \cdot 2H_2O$) (Pearson and McDonnell, 1975; Sverdrup, 1985; Lovell, 1973). When scaling occurs limestone reactors must incorporate unusually long hydraulic retention times (HRT) to compensate for reduced reaction rates (Maree et al., 1996; Ziemkiewicz et al., 1997) or use components capable of grinding or abrading limestone surfaces (Zurbuch, 1963; Lovell, 1973). The pulsed limestone bed (PLB) process has been developed (Watten, 1999) to accelerate limestone dissolution rates and to prevent the accumulation of solid reaction products. AMD is directed intermittently, through nozzles, into limestone sand reactors establishing a repeating cycle of fluidization, bed turnover and contraction. Abrasion of scale from limestone surfaces is provided by collision forces generated hydraulically during bed expansion. Further, a carbonation pretreatment step is used to accelerate limestone dissolution by forcing the reaction of calcite with $CO_2$ to form bicarbonate alkalinity,

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^- \tag{1}$$

and by minimizing, temporarily, the rise in pH that occurs during treatment so as to sustain the reaction of hydrogen ions with calcite, i.e.

$$CO_2 + H_2O = H_2CO_3 = H^+ + HCO_3^-, \tag{2}$$

$$CaCO_3 + H^+ = HCO_3^- + Ca^{2+}. \tag{3}$$

The reaction of calcite with $CO_2$ can become the primary mechanism of limestone dissolution at pH>4.7 (Plummer et al., 1978; Watten et al., 2004). Maintenance of high dissolved carbon dioxide (DC) levels within the reactor serves also to elevate equilibrium concentrations of $HCO_3^-$ (Stumm and Morgan, 1996) and thereby allow for surplus acid neutralization capacity in the reactor's effluent. DC not reacted away is stripped from the effluent to increase pH (Pearson et al., 1982), then is reused to minimize make-up $CO_2$ requirements (Watten, 1999; Sibrell et al., 2000).

Field tests of the PLB process (Sibrell et al., 2000; Sibrell and Watten, 2003) have demonstrated its ability to effectively treat AMD under conditions of moderate and extreme levels of Fe, Al and inlet acidity (Acy). Recent laboratory studies (Watten et al., 2005) conducted with a non-pressurized prototype of 60 L/min capacity showed effective removal of $H^+$ Acy over the range 196–584 mg/L ($CaCO_3$) while concurrently generating surplus acid neutralization capacity. Effluent alkalinity (Alk, mg $CaCO_3$/L) rose with increases in $CO_2$ (DC, mg/L) according to the model Alk $= 31.22+2.97\,(DC)^{0.5}$ where DC was varied from 11–726 mg/L. When HRT was held constant, altering the bed fluidization component of a repeating 60 s cycle (10, 20 or 30 s) did not influence Alk yields but did increase energy dissipation and bed expansion ratios. Numerical modeling showed $CO_2$ requirements are reduced as AMD Acy increases and when DC is recycled from system effluent. In a second pressurized reactor test series, Watten et al. (2004) correlated PLB performance with the variables reactor pressure ($P_{CO_2}$, 0–690 kPa), inlet Acy (6–1033 mg/L) and limestone bed height (27.3–77.5 cm). Effluent Alk here ranged between 36 and 1086 mg/L while operating with an HRT of just 4.2–5.0 min. Alk (mg/L $CaCO_3$) rose with increases in Acy and $P_{CO_2}$ according to the model: $Alk = a+b(P_{CO_2})^{0.5}+c(Acy)-d(P_{CO_2})^{0.5}(Acy)$ where a, b, c, and d are regression coefficients. The Alk observed represented less than 50% of equilibrium concentrations calculated with the aid of geochemical modeling software (Parkhurst, 1995) suggesting that increases in HRT could improve Alk yields. Further, temperature (T) may influence Alk yield given its effects on $CO_2$ and $HCO_3^-$ solubility as well as the reaction rate coefficients that govern limestone dissolution (Plummer et al., 1978; Sverdrup, 1985). The objective of the study described herein was to correlate PLB acid neutralization rate and effluent Alk with HRT, T and $P_{CO_2}$ so as to explore further the treatment potential of the process.

## 2. Methods

### 2.1. Test apparatus

We evaluated a PLB acid neutralization system capable of processing 15 L/min. Fig. 1 shows the system's major components—four 10 cm diameter × 203 cm vertical reaction columns charged with granular limestone, a 0.26 kW centrifugal pump (stainless steel) coupled with a 10 cm diameter × 203 cm packed tower carbonator and a time-based electronic control system (ChronTrol Corporation, San Diego, CA, USA) used to direct the system's electrically activated ball valves (Hayward Industrial Products, Inc., Elizabeth, NJ, USA). Reaction columns and the carbonator were designed as pressure vessels with transparent (PVC) walls. The carbonator was packed with 198 cm of Tellerette® type (47 mm × 19 mm) plastic packing with a specific surface area of 185 $m^2/m^3$. In operation, two of the four reaction columns (1 and 2 or 3 and 4) receive recycle water alternately from the carbonator, under pressure, to

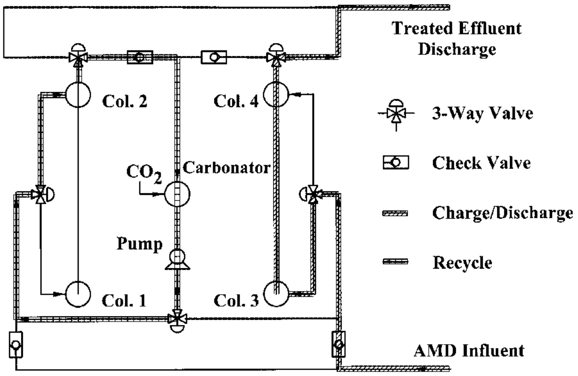

Fig. 1 – Plan view of the pulsed limestone bed AMD treatment system. In this example, limestone columns 1 and 2 are linked temporarily in a closed (treatment cycle) loop that includes a sealed packed tower carbonator. Within this loop recirculated AMD is directed alternately into each column at 1-min intervals. Concurrently, limestone columns 3 and 4 are receiving untreated AMD, alternately, at 1-min intervals during a temporary rinse/reloading cycle. The three-way valves shown are synchronized by a time-based control system that maintains a repeating 4-min cycle of rinse/reloading and treatment for each side of the system.

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