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Performance and application of a fluidized bed limestone reactor designed for control of alkalinity, hardness and pH at the Warm Springs Regional Fisheries Center

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ABSTRACT

Springs serving the Warm Springs Regional Fisheries Center, Warm Springs, Georgia, have pH, alkalinity, and hardness levels that lie under the range required for successful fish propagation while free CO_2 is well above allowable targets. We evaluate a pretreatment process that exploits limestone's ($CaCO_3$) ability to react away hydrogen ions (H^+) and carbon dioxide (CO_2) while increasing alkalinity (HCO_3^-) and calcium (Ca^{2+}) concentrations, i.e.

$CaCO_3 + H^+ \leftrightarrow HCO_3^- + Ca^{2+}$

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

Limestone sand was tested in both pilot and full scale fluidized bed reactors (CycloBio®).[1] We first established the bed expansion characteristics of three commercial limestone products then evaluated the effect of hydraulic flux and bed height on dissolution rate of a single selected product (Type A16 × 120). Pilot scale testing at 18C showed limestone dissolution rates were relatively insensitive to flux over the range 1.51–3.03 $m^3/min/m^2$ but were sensitive ($P < 0.001$; $R^2 = 0.881$) to changes in bed height (BH, cm) over the range 83–165 cm following the relation: (Alkalinity, mg/L) = 123.51 − (3788.76 (BH)). Differences between filtered and non-filtered alkalinity were small ($P > 0.05$) demonstrating that limestone was present in the reactor effluent primarily in the form of dissolved $Ca(HCO_3)_2$. Effluent alkalinity exceeded our target level of 50 mg/L under most operating conditions evaluated with typical pilot scale values falling within the range of 90–100 mg/L despite influent concentrations of about 4 mg/L. Concurrently, CO_2 fell from an average of 50.6 mg/L to 8.3 mg/L (90%), providing for an increase in pH from 5.27 to a mean of 7.71. The ability of the test reactor to provide changes in water chemistry variables that exceeded required changes allowed for a dilution ratio of 0.6. Here, alkalinity still exceeded 50 mg/L, the CO_2 concentration remained well below our limit of 20 mg/L (15.4 mg/L) and the pH was near neutral (7.17). Applying the dilution ratio of 0.6 in a full scale treatment plant at the site reduced by 40% the volume of spring water that is directed through each of three parallel reactors that combined react away 49,000 kg of limestone/yr.

1. Introduction

The Warm Springs Regional Fisheries Center (WSFC), Warm Springs, Georgia, relies primarily on the facility's Cold Spring (18C) to provide water required for hatchery and pond production of sunfish (Centrarchidae), catfish (Ictaluridae), bass (Moronidae), sturgeon (Acipenseridae) and redhourse (Catostomidae). Spring output is about 3 m^3/min which is supplemented, when needed,

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[1] Any use of trade, product or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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by a lower capacity (0.7 m^3/min) South Spring. Both springs have chemistries that are similar but lie outside the range required for successful fish propagation (Boyd, 1990; Piper et al., 1982). Of primary concern is an elevated carbon dioxide concentration (>35 mg/L) that, following the bicarbonate buffer system (Stumm and Morgan, 1985), acts along with a low ambient concentration of alkalinity (<4 mg/L as $CaCO_3$) to create an acidic pH (5.1). Acidic waters interfere with ion balance as well as produce hypertrophy of gill chloride and epithelial cells. Both effects are linked to increases in mortality (Menendez, 1976; Flik et al., 1995; Packer and Dunson, 1970; Ingersoll et al., 1990). Elevated carbon dioxide concentrations can cause stress, reduced growth, and nephrocalcinosis (Smart et al., 1979; Basu, 1959; Ross et al., 2001; Danley et al., 2005). Sufficient akalinity/hardness is required to avoid unacceptable swings in pH as well as to support maintenance of adequate internal Ca^{2+} pools needed for ion balance, bone construction and moderation of the toxicity of certain metals, nitrite and ammonia (Tomasso et al., 1980; Townsend et al., 2003; Flik et al., 1986; Grizzle and Mauldin, 1994; Miller and Mackay, 1980). The WSFC targets for water chemistry are: pH, 6.5–7.5; carbon dioxide, 20.0 mg/L; alkalinity, 50 mg/L; hardness, 50 mg/L. Early treatments (1952) at WSFC were based on application of agricultural limestone directly to rearing ponds. The application of 1120 kg/ha had little effect on water chemistry but applications of 11,120 kg/ha did improve pH, hardness and fish yields (Boyd, 1990). Currently, the South Spring is meeting water quality targets through the continuous dosing of three chemical reagents as a pretreatment – (1) sodium hydroxide for pH and carbon dioxide control, (2) sodium bicarbonate for alkalinity addition, and (3) calcium chloride for hardness control. Although the treatment has been effective, reagent costs are substantial. The WFSC Cold Spring water has more recently been preconditioned by blending a less expensive hydrated lime slurry in a side-stream loop. Piping involved in the loop, unfortunately, is prone to blockage by the rapid development of calcium based scale with associated and unacceptable levels of labor input. Fluidized bed reactors charged with limestone sand (Watten et al., 2004) have potential for reducing pretreatment costs at WSFC given the sands market value, on an equivalent basis, is a fraction (0.03–0.26) of the alternative reagents (Hedin et al., 1994). Limestone use in the reactor will cause a rise in pH, alkalinity and hardness as H^+ and CO_2 react away to form calcium bicarbonate as per the stoichiometry below:

$$CaCO_3 + H^+ \leftrightarrow HCO_3{}^- + Ca^{2+} \tag{1}$$

$$\mathrm{HCO_3{}^- + H^+ \leftrightarrow H_2CO_3 \leftrightarrow H_2O + CO_2} \tag{2}$$

$$\mathrm{CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2\,HCO_3{}^-} \tag{3}$$

$$\mathrm{CaCO_3 + H_2O \leftrightarrow Ca^{2+} + HCO_3{}^- + OH^-} \tag{4}$$

The reaction of calcite with CO_2 (Equation (3)) can be the primary mechanism of dissolution at pH >4.7 (Plummer et al., 1978; Watten et al., 2004). Maintenance of high dissolved carbon dioxide levels within a reactor can serve also to elevate equilibrium concentrations of $HCO_3{}^-$ (Stumm and Morgan, 1996) and thereby allow for surplus acid neutralization capacity in the reactors effluent. Hence, reactors are designed to minimize CO_2 off gassing during treatment and in some cases a carbonation pretreatment step is combined with pressurization to increase and maintain high levels of CO_2 within the reactor (Watten, 1999; Watten et al., 2005; Watten et al., 2007). CO_2 not reacted away is stripped from solution to increase pH then is reused, in some cases, to minimize make up CO_2 requirements (Watten et al., 2004; Sibrell et al., 2005). Sibrell et al. (2006) carbonated low pH/low alkalinity water prior to treatment with a fluidized limestone bed reactor at the Craig Brook National Fish Hatchery, East Orland, Maine. Reactor dimensions were 203 × 30 cm ID with an effective hydraulic flux of 0.54 $m^3/min/m^2$. Effluent alkalinity rose with dissolved CO_2 following the relationship: alkalinity (mg/L) = 72.84 × $P(CO_2)^{0.5}$ where $P(CO_2)$ is kPa. Application of the model suggests the high CO_2 present in the WFSC water supply is sufficient, without additional carbonation, to provide reactor effluent alkalinity concentrations that would allow for side-stream blending. This operating mode is attractive given linked reductions in reactor scale (capital) and energy (pumping) requirements. The Sibrell et al. (2006) study, however, evaluated limestone obtained from a quarry site in central Pennsylvania. Limestone sand composition and particle size distributions will vary with source and can influence dissolution rate (Eisenlohr et al., 1999; Shih et al., 2000; Toprac and Rochelle, 1982). Sand particle size distributions will also affect the hydraulic flux required for target bed expansion ratios that, in turn, control reactor dimensions (Cleasby, 1990; Summerfelt, 2006). In our current tests we establish the bed expansion characteristics of three commercial limestone products quarried near the WSFC then evaluate the effect of hydraulic loading on dissolution rate of a single selected product, including the potential for side-stream treatment with blending. We also correlate reactor performance with changes in bed height that occur during long-term operation. Performance and dissolution rate tests were conducted at a pilot scale and full scale using a proprietary reactor type (CycloBio®, Marine Biotech) as described by Summerfelt (2006). Here water is introduced tangentially into an annular manifold molded within the base of the reactor. Water enters the fluidized bed compartment through a slot present along the circumference of the bed. An inverted cone, molded into the base of the reactor, is used to redirect the flow vertically so as to establish bed expansion as well as cyclonic rotation.

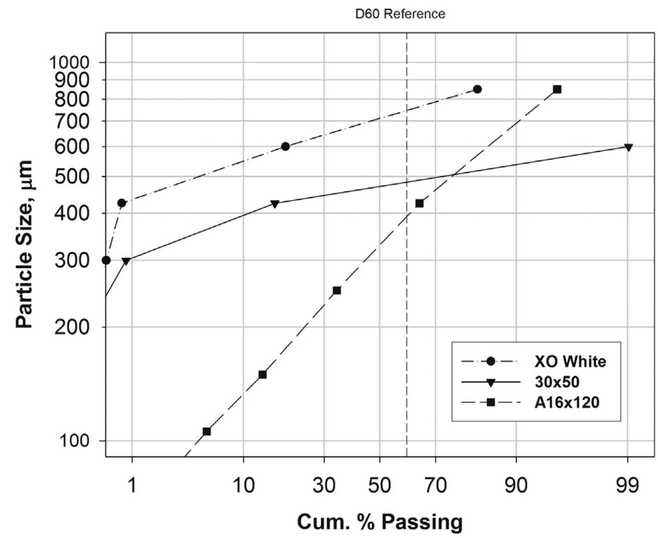

Fig. 1. Particle Size Distributions for Limestone Sand Products Tested in Test Series I.

2. Test methods

2.1. Test series I – limestone sand fluidization characteristics

Bed expansion characteristics were established for each of three local limestone products using a vertical section of clear PVC pipe measuring 233.7 × 10.2 cm ID that served as the fluidized bed reactor. The limestone samples evaluated were IMERYS types 30 × 50 and XO White (Roswell, Georgia), and Franklin Industrial Minerals Group type A16 × 120 (Nashville, Tennessee). Fig. 1 gives particle size distributions we established for each product type using standard sieve procedures (Summerfelt, 2006). Domestic water was directed into the base of the test column, charged previously with