Sustained Treatment of AMD Containing Al and Fe^{3+} with Limestone Aggregate

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Abstract Acid mine drainage with pH 3.0 and containing 27 mg/L Al, 10 mg/L Fe, and 15 mg/L Mn was treated experimentally for 2+ years with high calcite limestone aggregate in 23 m^3 boxes equipped with programmable flushing devices. A variety of flow regimes and flushing modes were tested. The best sustainable treatment occurred when AMD flowed vertically down through flooded limestone aggregate and the bed was drained empty once a week. One box operating in this mode has produced an alkaline discharge with low Al, Fe, and Mn for 560 days with minimal maintenance.

Key Words acid mine drainage, passive treatment, limestone

Introduction

Limestone is a preferred reagent for the treatment of acid mine drainage (AMD) produced by coal mining for several reasons. It is usually available in coal-producing regions and is substantially less costly than chemical alternatives like CaO, $Ca(OH)_2$, NaOH, and Na_2CO_3. It is not caustic and can be handled and stored without safety concerns. It has a limited solubility which makes possible the installation of years of treatment capability at a single time. Despite these advantages, limestone's use in AMD treatment has been limited because of problems associated with sustaining its reactivity and, when used in an aggregate manner, maintaining permeability. The most successful use of limestone aggregate in AMD treatment is the anoxic limestone drain (ALD), but this application is limited to waters that do not contain aluminum (Al) and ferric iron (Fe^{3+}) (Hedin et al. 1994). Treatment techniques have been developed that utilize limestone aggregate for these waters, but each has its problems. Channels filled with limestone aggregate (OLCs) can provide sustainable acidity neutralization, but do not produce an alkaline effluent (Ziemkeiwic et al. 1997). Vertical flow ponds (VFP) utilize organic substrates and plumbing to counteract problems with Al and Fe^{3+} and, when properly implemented, produce a high quality effluent (Rose and Dietz 2002; Hedin et al., in press). However, the high capital cost and land requirements of VFP systems can be problematic.

This paper presents the results of experiments involving the treatment of a high-Al AMD with limestone aggregate under oxic conditions. The project was intended to 1) elucidate the problems associated with the treatment of these waters with limestone aggregate, 2) develop low-tech procedures that would avoid these problems, and 3) determine whether a system designed with these features could consistently discharge a high quality effluent without major maintenance requirements.

Study Site and Methods

The research project was conducted at the Anna S Deep Mine Complex in Tioga County, Pennsylvania, USA. The underground coal mine has been abandoned since the early 1900s and has produced AMD with low pH and elevated concentrations of Al and Fe for decades. Three discharges from the mine are treated with a large passive treatment system that is described elsewhere (Hedin et al. in press). A fourth discharge, referred to as Mitchell, was targeted for treatment by this project.

Two identical experimental limestone units were constructed (East Box and West Box). Table 1 shows unit dimensions and contents. The boxes received a piped AMD influent that discharged on top of the limestone bed. The effluent from each unit was collected at the box bottom and piped to a device that controlled the water level in the boxes and also was used to rapidly empty the bed. The empting of each box was controlled by a programmable computer (AgriDrain Smart Drainage System, www.agridrain.com/sds.html).

The boxes received the same influent mine water, but otherwise operated independently. Parameters that could be varied included: inflow rate, inflow distribution pattern, water depth in the limestone bed, flush longevity, and flush trigger. The triggering of a flush event was controlled by the computer which could be programmed to act on time or water depth in the box. For some tests the boxes were set up with identical operational parameters and treated as replicates. For

Table 1 *Construction and summary treatment statistics for the two experimental limestone systems*

	West Box	East Box
Box dimensions	6.6 m by 2.2 m by 1.6 m (identical)	
Limestone depth and mass	1.3 m deep, 30 tonnes (identical)	
Limestone $CaCO_3$ content , gradation,	98% $CaCO_3$, 12.7 mm-25.4 mm, (identical)	
Duration of operation	917 days (ongoing)	419 days
Flow rate average (range)	2.7 L/min (1.9-20.8 L/min)	3.2 L/min (1.9-20.8 L/min)
Total mass limestone dissolved	2.5 tonnes	1.9 tonnes
Total mass Al removed	205 kg	163 kg
Total mass Fe removed	58 kg	39 kg
Total mass Mn removed	53 kg	47 kg

other tests, one operational parameter was varied and the importance of the parameter was determined by comparing treatment effectiveness between the boxes. Effectiveness was measured by comparing influent and effluent chemistry and loading. Flow rates were measured at the box influents and used to calculate loadings. Details of the project are available in the final report (Hedin Environmental 2008).

Results and Discussion

The dual goals of acid mine drainage treatment are the neutralization of acidity and the precipitation of dissolved metals. In oxic limestone beds calcite dissolution neutralizes acidity and promotes the formation of Al and Fe solids through pH-dependent hydrolysis processes. To maximize the reactions, the contact time between limestone and the AMD should be maximized. Much of the solids precipitation occurs within aggregate void spaces. These voids provide flow paths through the aggregate and if the solids are not managed, permeability restrictions will eventually cause preferential flow and lessen contact between AMD and limestone. The solids can be managed (removed) with high velocity flushing, but flushing events decrease contact time between the AMD and limestone because during the filling cycle half of the limestone is not in contact with AMD.

Types of Metal Solids

Two types of metal solids formed in the limestone beds. Solids accumulated in the pore water within the aggregate void spaces creating a white liquid with high suspended solids content. It is hypothesized that these highly turbid zones formed when alkaline water created by calcite dissolution mixed with low-pH water containing Al and hydroxide solids were formed in situ. These suspended solids were removed by draining water from the pore spaces during flushing. A second type of solids occurred that was associated with individual limestone stones. These solids formed a scale on the exposed stone surface and are hypothesized to be a result of metal hydrolysis reactions very close to the calcite surface. The scale was brittle and flaked off the stone naturally, which exposed a fresh limestone surface. Attached and dislodged scale was found throughout the limestone bed. Flushing did not provide enough energy to move scale out of the bed.

Flushing and Treatment Performance

To determine the effects of flushing on treatment performance, an experiment was conducted where the West Box was operated without flushing while the East Box was flushed empty twice per week. All other operational parameters were the same for the two boxes. Figure 1 shows the % decrease in acidity ((influent – effluent)/influent) where >100% removal occurred when the effluent was net alkaline. Before the experiment the boxes performed similarly. Five days following the cessation of flushing for the West Box, its effluent quality had improved dramatically. The improvement was attributed to the increase in contact time between the AMD and limestone in the continuously flooded box. The superior performance was shortlived as the performance of the West Box steadily declined over the next 60 days. After the experiment was terminated and flushing of the West Box resumed (day 183), its performance rebounded and on day 215 the boxes performed equivalently.

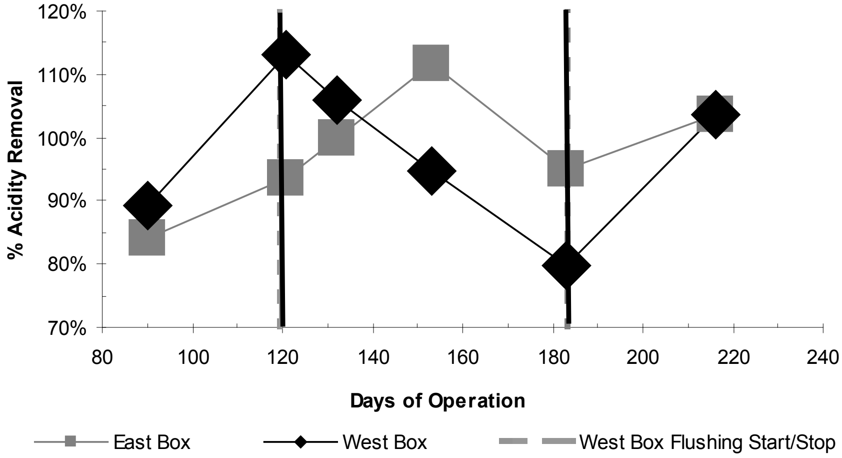

***Figure 1** Acidity removal by the experimental limestone boxes with and without (West Box only) flushing*

Long-term Treatment by the West Box

Experiments that varied loading rates, influent distribution, and flushing frequency resulted in a prediction that the limestone units could sustainably treat 3—4 L/min of flow when set up to operate in a flooded condition with once/week emptying. The West Box has operated under these conditions since Oct 2008 and has produced a net alkaline discharge on every sampling date. Table 2 shows the average influent and effluent chemistry. The consistent removal of Mn was unexpected. With a small settling basin to remove particulate Al, the system's final discharge would satisfy most NPDES limits.

Metal Solids Removal by Flushing

Metal budgets were developed for the boxes by calculating the total mass input of individual metals, the mass output under routine (non-flush) operation and during flush events. Table 3 shows average partitioning for Fe and Al for the West Box in 2008 and also a single measurement in April 2010 when it had been operating with minimal oversight for the previous 16 months. In 2008, the boxes discharged 8% of the influent Fe and 15% of the influent Al during routine (non-flush) operations. The Fe and Al discharged during routine operation were particulate which can be easily settled. The remaining Fe and Al solids were retained in the limestone bed. During the flush events, 35—41% of the influent Fe and Al loading were discharged from the boxes. During a complete treat/flush cycle the West Bed retained 51% of the influent Fe and Al load. The Fe and Al solids retained in the boxes are hypothesized to be high density scales.

In 2010 the West Box was found to be managing solids similarly to 2008. Approximately 40% of the Al and Fe loading was flushed from the bed and 56% was retained.

***Table 2** Average (n=13) influent and effluent chemistry for the West Box, Oct 2008 – Apr 2010. "na" indicates data not available*

	Flow L/min	pH	Acidity mg/L $CaCO_3$	Al^{tot} mg/L	Fe^{tot} mg/L	Mn^{tot} mg/L
Influent	3.2	3.0	246	27.2	9.7	14.6
Effluent	na	6.9	-60	2.6	0.6	2.8

***Table 3** West Box Fe and Al removal and retention.*

Date	Fe Flushed	Fe Discharged	Fe Retained	Al Flushed	Al Discharged	Al Retained
2008 average (n=7)	40.6%	8.3%	51.1%	34.4%	14.7%	50.9%
April 20, 2010	41.6%	4.6%	53.8%	37.8%	4.4%	57.8%

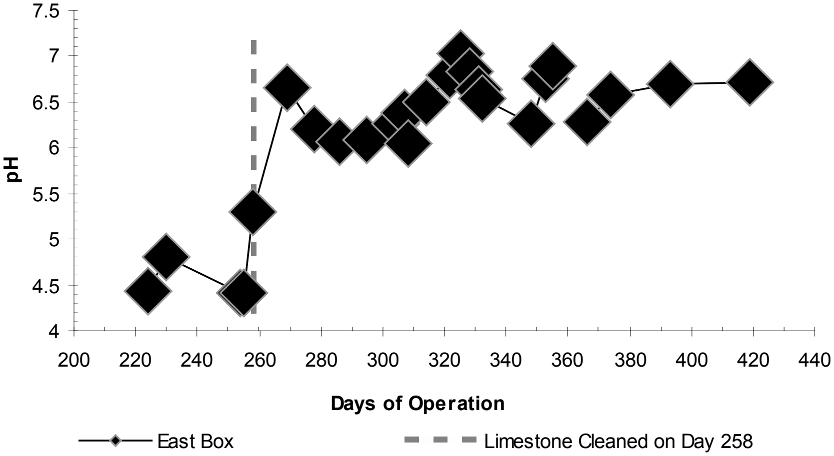

Figure 2 *East Box effluent pH before and after limestone cleaning*

Mechanical Removal of Scale

The accumulation of scale solids within the limestone aggregate is likely to eventually cause decreased treatment effectiveness. Several aggregate cleaning experiments were conducted. Scale was readily removed from the limestone surface by physical agitation with an excavator combined with a continuous flow of water (AMD) that transported solids away from the stone. Scaled limestone aggregate was cleaned in 2007 at a cost of $3/tonne.

Figure 2 shows the pH of the effluent of the East Box before and after the aggregate was cleaned. Before cleaning the box effluent had pH 4.3 – 4.8. After the limestone was cleaned, the effluent pH increased to 6.5 and maintained this condition until the box was dismantled 160 day later.

Conclusions

Limestone aggregate can provide effective low-maintenance treatment of AMD containing Al when the solids are managed. Specifically, solids accumulating in pore waters within the limestone aggregate must be periodically removed. Emptying the bed once/wk provides adequate solids management. Metal solids that form scale directly on limestone surfaces do not substantially degrade calcite dissolution over periods of 2—3 years. If the scale becomes problematic, it can be easily removed with an excavator and pump at a cost much less than limestone replacement. These results provide the basis for a method for treating AMD containing high Al and Fe^{3+} with limestone.

Acknowledgements

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