CASE STUDY

Penn State University Laboratory Bench-Scale Research Passive Remediation of Acid Mine Drainage

August 2010

Prepared by
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Mining Waste Team

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ITRC (Interstate Technology & Regulatory Council). 2010. *Penn State University Laboratory Bench-Scale Research, Passive Remediation of Acid Mine Drainage*. Mining Waste Treatment Technology Selection Web. Washington, D.C.: Interstate Technology & Regulatory Council, Mining Waste Team. www.itrcweb.org.

Acknowledgements

The ITRC Mining Waste Team would like to acknowledge JRW Bioremediation, LLC and Rachael Brennan from Pennsylvania State University, who completed the April 2008 Mine Waste Case Study Survey, from which the information in this case study is taken.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

PENN STATE UNIVERSITY LABORATORY BENCH-SCALE RESEARCH PASSIVE REMEDIATION OF ACID MINE DRAINAGE

1. SITE INFORMATION

1.1 Contacts

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1.2 Name, Location, and Description

This case study reviews the main results of investigation into a novel concept for treating streams contaminated by acid mine drainage (AMD) using a multifunctional substrate: chitin from crab shells. Researchers have been concerned about the acidic metal–laden drainage from abandoned coal mines because of the serious threat to humans, wildlife, and exposed structures. Particularly, north central Pennsylvania surface water has been affected by coal mining activities, which began in the mid-1700s. Over 10 billion tons of bituminous coal has been mined in 21 Pennsylvania counties during the past 200 years, about one-fourth of all coal ever mined in the United States. Ranked in order of production, the counties containing coal mines are Greene, Somerset, Armstrong, Indiana, Clearfield, Washington, Cambria, Jefferson, Westmoreland, Clarion, Elk, Fayette, Lycoming, Butler, Lawrence, Centre, Beaver, Blair, Allegheny, Venango, and Mercer. Early mining companies did not have the technology or knowledge to realize the long-term effects of mining. Therefore, the hundreds of years of coal mining in Pennsylvania have left the descendents of coal miners over 2,400 miles of streams polluted by AMD from abandoned mining operations.

To test chitin from crab shells as a method of AMD treatment, samples of surface water, sediment, and soils were taken in Kittanning Run approximately 2.7 miles downstream of the nearest coal mine (latitude 40.49781N, longitude 78.47633W), in Blair County, Pennsylvania (Figure 1-1). Laboratory studies were conducted by Dr. Rachel Brennan of the Penn State University Department of Civil and Environmental Engineering.

Figure 1-1. Kittanning Run sample point for surface water.
(*Source:* GoogleEarth 2009 with a satellite image of June 2005. *Elaboration:* ITRC.)

2. REMEDIAL ACTION AND TECHNOLOGIES

Because of AMD’s environmental and public health effects, many technologies have been investigated to treat, reduce, and/or wipe out AMD sources. One of the most widespread technologies is passive anaerobic treatment, such as vertical flow wetlands and permeable reactive barriers. These systems simultaneously increase alkalinity and remove metals by supporting the activity of sulfate-reducing bacteria (SRB). Recent investigations demonstrated that slow-release and fermentable substrates most suitable for use in these systems are typically deficient in nitrogen, which is a limiting factor for SRB growth (Waybrant 2002, cited in Daubert and Brennan 2007). In consequence, the design of the passive treatment systems is often greater than the necessary, due to SRB organic requirements. This work investigated a novel concept for treating AMD in which the biological reduction of acidity, chemical enhancement of alkalinity, and physical sorption of metals occurred simultaneously.

Chitin, with a chemical formula of $C_8H_{13}NO_5$, is the second most abundant biopolymer on Earth after cellulose (Beaney 2005, cited in Daubert and Brennan 2007). Its chemical nitrogen content is 6.9%, which gives it the ideal carbon:nitrogen relation to support SRB development. Furthermore, it is attractive due to its slow-release substrate and because of its fermentation in hydrogen, acetate, and a variety of other fatty acids (Vera et al. 2001, cited in Daubert and Brennan 2007). What’s more, chitin is an excellent physical sorbent, especially at low pH, and has been shown to remove metals like aluminum, arsenic, chromium, copper, iron, manganese, nickel, and zinc from aqueous solutions. To sum up, chitinous materials can be effectively used for AMD remediation, likely due to its ability to simultaneously serve as an electron donor source (volatile fatty acid), nitrogen source (ammonium), and neutralizing agent ($CaCO_3$) to sustain SRB activity.

To compare the efficiency of distinct carbon substrates, a series of mushroom compost, sodium lactate, ChitoRem® chitin complex (CRCC), and ChitoRem® chitin complex plus a biological nutrient were tested with the AMD sampled in Kittanning Run. Daubert and Brennan (2007) describe the method used to test the chitin substrate. The other substrates were tested by a similar method, summarized as follows. Water samples were degassed with nitrogen in the collection vessels for 90 minutes to ensure low dissolved-oxygen conditions. During this time, 0.5 g of soil and 0.25 g of each substrate were added to a series of replicates of 160 mL glass serum bottles. Control bottles without substrate were also established. Degassed AMD water was then transferred to each bottle anaerobically in 100 mL aliquots, and the bottles were sealed with butyl rubber stoppers and aluminum crimp tops. The bottles were shaken by hand to mix the sediment and chitin, prior to incubating in the dark at room temperature until analysis. Duplicate bottles were sacrificed daily until changes in pH and acidity stabilized.

3. PERFORMANCE

AMD water samples were treated in the presence of each substrate, showing the performance detailed in Table 3-1 and Figures 3-1 and 3-2. As it can be seen, after 27 days, pH increased in all cases from acid to near neutral. The best performance was obtained in the CRCC test, with a pH of 7.75. Alkalinity reached good levels in the cases of chitins from below the limit of detection (<LOD) to 785 and 900 mg/L for CRCC and CRCC-enriched, respectively, indicating the presence of carbonate and hydroxyl groups leached from each substrate, giving them basic character. At the same time, a decrease of the sulfate concentration can be observed due to the demand of oxygen from SRB to transform it into sulfide. The lowest sulfate concentration corresponds to CRCC-enriched which, after 27 days, decreased from 980 to 29 mg/L.

Table 3-1. Results after 27 days of applying AMD surface water to different substrates

Parameter	Initial condition	Mushroom compost	Sodium lactate	ChitoRem® chitin complex (CRCC)	CRCC plus a biological nutrient
pH	2.95	5.48	5.04	7.75	7.47
Alkalinity	<LOD[a]	17.5	105.5	785.5	900.0
Sulfate, mg/L	980	623	712	118	29
Iron, mg/L	10.00	<LOD	16.00	<LOD	<LOD
Al, mg/L	10.00	<LOD	7.00	<LOD	<LOD
Mn, mg/L	15.00	16.50	17.00	4.45	5.10
Zn, mg/L	0.63	0.05	0.39	<LOD	<LOD

[a] <LOD = below the limit of detection.

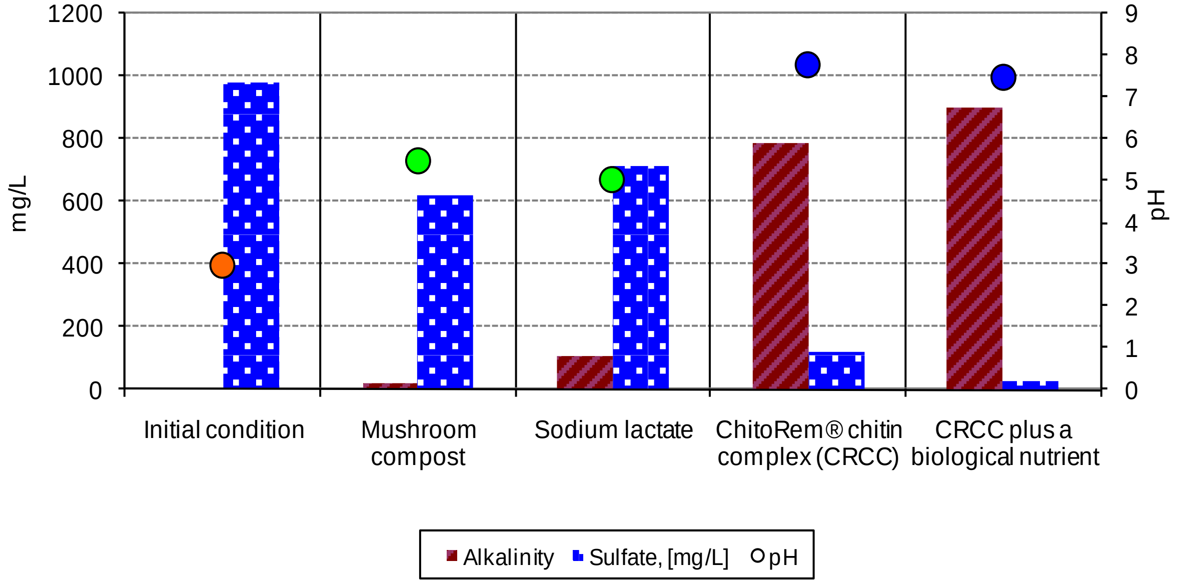

Figure 3-1. pH, alkalinity, and sulfate parameters after 27 days of testing.
(*Source:* Robinson-Lora and Brennan 2009. *Elaboration:* ITRC.)

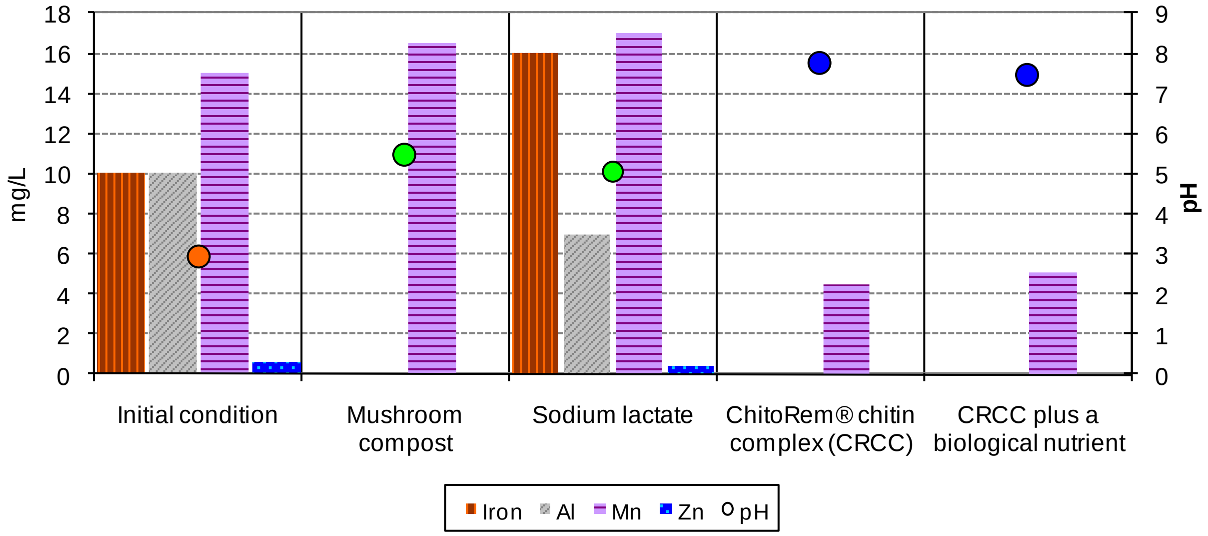

Figure 3-2. Iron, aluminum, manganese, and zinc parameters after 27 days of testing.
(*Source:* Robinson-Lora and Brennan 2009. *Elaboration:* ITRC.)

Based on the concentration of heavy metals in each substrate (Figure 3-2), it can be seen that CRCC and CRCC-enriched are an ideal media to precipitate heavy metals as sulfides. Zinc, as an indicator to form sulfides, reached a <LOD level in chitin and mushroom substrates. In dependence of increasing in pH, iron (Fe), aluminum (Al) and manganese (Mn) form hydroxides. Mushroom and chitin test demonstrate a precipitation of iron and aluminum as $Fe(OH)_3$ and $Al(OH)_3$ due the pH (around 5–8). However, manganese remains soluble in the four substrates,

with a reduction of about 3 times less than the initial condition in the case of chitin substrates, which is in direct dependence of the solubility product of manganese hydroxide (MnOH) as function of the increase of pH. It is important to point out that MnOH rapidly transforms into MnO_2, which is practically insoluble at any pH.

In conclusion, the results of this work demonstrate the effectiveness of chitin as an alternative substrate for AMD treatment.

4. COSTS

Capital cost for this study was estimated to be less than \$0.002/gallon, or \$0.404/cubic yard.

Operation and maintenance cost was not estimated because experiments were conducted in a batch test.

5. REGULATORY CHALLENGES

The application of the test was driven under Clean Water Act and Comprehensive Environmental Response, Compensation, and Liability Act regulations. The results of laboratory test met or exceeded maximum contaminant levels and determine lowest possible cleanup levels.

6. STAKEHOLDER CHALLENGES

The results of the application of the technology demonstrated that it can be used in an engineered wetland as a contained bioreactor or possibly as a directly injected biobarrier. These uses will require that a treatment area or zone be established and maintained throughout the length of the project.

7. OTHER CHALLENGES AND LESSONS LEARNED

The process includes both biological and chemical components that were difficult to differentiate in the initial part of the tests. This distinction requires further investigations through the performance of an on-site pilot-scale test. Substrate longevity could also not be determined due to the limited samples size but was estimated to exceed two years, based on comparison of this data with other chitin complex microcosm and field data.

8. REFERENCES

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