

# **Report as of FY2006 for 2006PA63B: "Passive Remediation of Acid Mine Drainage Using Chitin"**

## **Publications**

- Water Resources Research Institute Reports:
  - Brennan, R.A. (2007), Passive remediation of acid mine drainage using chitin, PA WRRI, The Pennsylvania State University, University Park, PA, 5 pp.
- Articles in Refereed Scientific Journals:
  - Daubert, L.N. and R.A. Brennan (2007) Passive remediation of acid mine drainage using chitin. Environmental Engineering Science (in press).
- Dissertations:
  - Daubert, L.N. (2006) B.S. Honors Thesis, A laboratory investigation of passive remediation of acid mine drainage using chitin from crab shells. Department of Civil and Environmental Engineering, College of Engineering, The Pennsylvania State University, University Park, PA.
  - Robinson, Lora, M.A., Ph.D. Dissertation, Department of Civil and Environmental Engineering, College of Engineering, The Pennsylvania State University, University Park, PA (in progress).

## **Report Follows**

## **PRINCIPAL FINDINGS AND SIGNIFICANCE**

Streams contaminated by acid mine drainage (AMD) are complex environmental systems which require biological, chemical, and physical treatment steps for thorough remediation. In this work, a novel concept for treating AMD was investigated, in which the biological reduction of acidity, chemical enhancement of alkalinity, and physical sorption of metals occurred simultaneously using one multifunctional substrate: chitin from crab shells. In this research, crab shell chitin was evaluated as an alternative substrate for the treatment of acid mine drainage in both microcosm and column experiments.

Sacrificial duplicate microcosms were used to rapidly assess the ability of chitin to achieve remediation of AMD waters of varying acidity and metals contents. For use in these tests, AMD source water and benthic sediments were collected from three sites in Centre County, Pennsylvania: Beech Creek (BC); North Fork (NF); and Cherry Run (CR) (Figures 1 and 2). Microcosms were setup under anoxic conditions in 160-ml glass serum bottles containing 120-ml AMD water, 0.5-g sediment, and 0.25-g SC-20 chitin (Figures 3 and 4). Duplicate control microcosms without chitin were also setup. The bottles were incubated in the dark at room temperature and monitored periodically for pH, alkalinity, acidity, sulfate, and metals concentrations for 20 days. Continuous-flow column studies were then conducted to quantify sulfate reduction rates, metal removal capacities, substrate longevity, and optimal retention times when crab shell chitin was used as a barrier material for AMD treatment. Duplicate, clear PVC tubes measuring 4-ft in length and 1.5-inches in diameter were packed with a mixture of 500-g silica sand, 50-g soil, and 25-g chitin in the first 1 foot segment, and silica sand for the remaining 3 feet (Figure 5). A control column without chitin was also evaluated. Water from an AMD site was pumped through the columns vertically from bottom to top at a rate of 0.25 ml/min and monitored until metals were observed to breakthrough in the effluent. At the conclusion of the experiment, the columns were sacrificed and the sediment analyzed for precipitated metal concentrations as a function of distance throughout the columns.

Results from this study showed that in the presence of crab shell chitin, acidity decreased, pH and alkalinity increased, and dissolved metals decreased. In the microcosm tests, chitin increased the pH from 3.5 to near neutral in just 2 days. Steady alkalinity generation and acidity removal were observed at an average rate of 37.6 mg CaCO<sub>3</sub>/L-d. The activity of sulfate reducing bacteria was evident after 8 days of incubation at reduction rates of 12 – 24 mg SO<sub>4</sub><sup>2-</sup>/L-d. No significant differences in performance were observed between the three evaluated sites. In the column tests, a retention time of 11.2 hours was enough to raise the pH from ≤ 3.5 to approximately 7.5. Alkalinity was generated at a rate of 48 ± 18 mg CaCO<sub>3</sub>/d, and acidity was removed at a rate of 64 ± 23 mg CaCO<sub>3</sub>/d. Greater than 95% of manganese, iron, and aluminum were removed from the water for 80, 109, and 125 days, respectively. Approximately 50 - 64% of the influent sulfate was removed throughout the column experiment. Physical adsorption of iron to chitin, chemical precipitation of aluminum hydroxide (Al(OH)<sub>3</sub>), and biologically induced manganese sulfide (MnS) precipitation were the likely mechanisms of dissolved metals removal in this system.

This study demonstrated that crab shell chitin is a promising substrate for AMD treatment. Dissolution of calcium carbonate from chitin promotes rapid pH, alkalinity, and acidity changes, independent of the sites' characteristics. The activity of sulfate reducing bacteria is enhanced by the addition of chitin as a substrate. Metals can be effectively removed from AMD waters by physical sorption and precipitation in less than 12 hours of continuous flow treatment with chitin. The longevity of chitin in the column tests indicates that in general, approximately 1 liter of AMD water can be treated per gram of raw crab-shell chitin.

## **STUDENTS SUPPORTED** (name, major, degree)

Linda Daubert\*, B.S., Chemical Engineering

Mary Ann Robinson Lora, Ph.D., Environmental Engineering

(\*No financial support, but participated early in the study in the form of an Honors Thesis.)

## **PRESENTATIONS AND OTHER INFORMATION TRANSFER ACTIVITIES**

Daubert, L. and R. A. Brennan. (2006) "A laboratory investigation of passive acid mine drainage treatment using chitin." *Poster presentation (1st Place Winner in Engineering category)*, Undergraduate Research Exhibition, The Pennsylvania State University, University Park, PA, April 5.

Robinson Lora, M. A. and R. A. Brennan. (2007) "Passive remediation of acid mine drainage using chitinous materials: microcosm and column studies on three sites within central Pennsylvania." *Poster presentation (2nd Place Winner in Engineering category)*, The Graduate Exhibition, The Pennsylvania State University, University Park, PA, March 25.

Robinson Lora, M. A. and R. A. Brennan. (2007) "Natural chitinous material as a neutralizing agent and electron donor source for the passive remediation of acid mine drainage." *Poster presentation*, 10th Annual Environmental Chemistry Student Symposium, The Pennsylvania State University, University Park, PA, April 13.

Daubert, L. N., and R. A. Brennan. (2007) "Passive remediation of acid mine drainage using chitin." *Platform presentation*, In Situ and On-Site Bioremediation 9th International Symposium, Baltimore, MD, May 7.

## **AWARDS**

Daubert, L. N., 1<sup>st</sup> place winner for poster presentation at the Undergraduate Research Exhibition, April 2006 (see citation above).

Robinson Lora, M. A., 2<sup>nd</sup> place winner for poster presentation at The Graduate Exhibition, March 2007 (see citation above).

## **ADDITIONAL FUNDING ACQUIRED USING USGS GRANT AS SEED MONEY**

Source: National Science Foundation  
Start date: February 15, 2007  
End date: December 31, 2011  
Title: CAREER: Solving a Global Water Crisis in a Local Watershed: A Comprehensive Analysis of Chitin as a Multifunctional Substrate for the Treatment of Acid Mine Drainage.

FIGURES

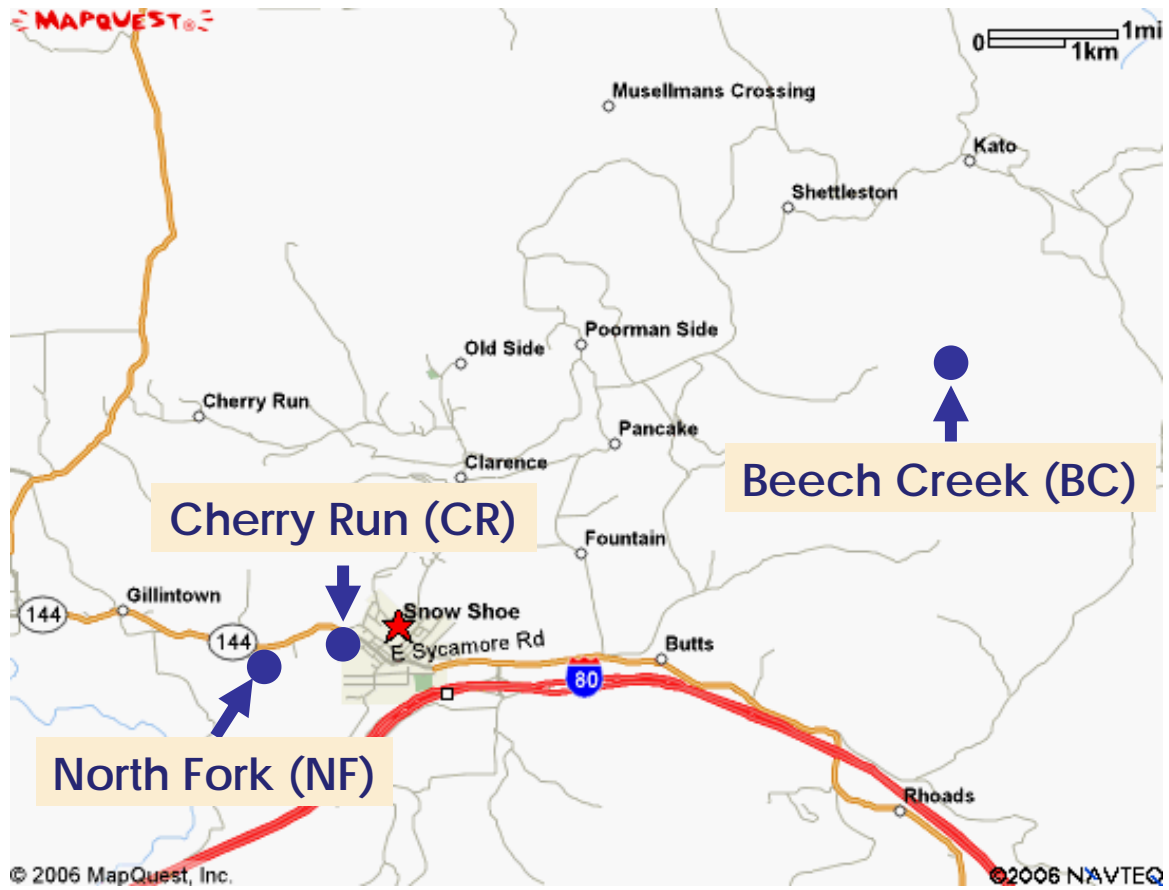


Figure 1. Map of AMD sampling sites in Centre County, PA (Source [www.mapquest.com](http://www.mapquest.com)).



Figure 2. Photograph of Beech Creek, PA, one of the selected sampling sites.

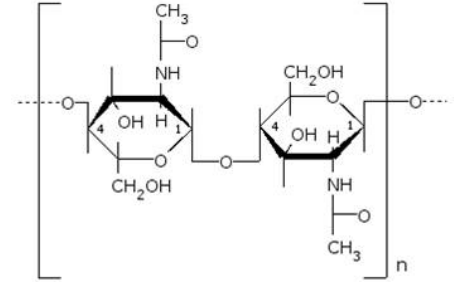


Figure 3. From left to right: a crab, the main source of commercially available chitin; processed SC-20 grade crab shells to be used in this study; and the chemical structure of two chitin monomers (N-acetylglucosamine, NAG) connected by a  $\beta$ -1,4-linkage.

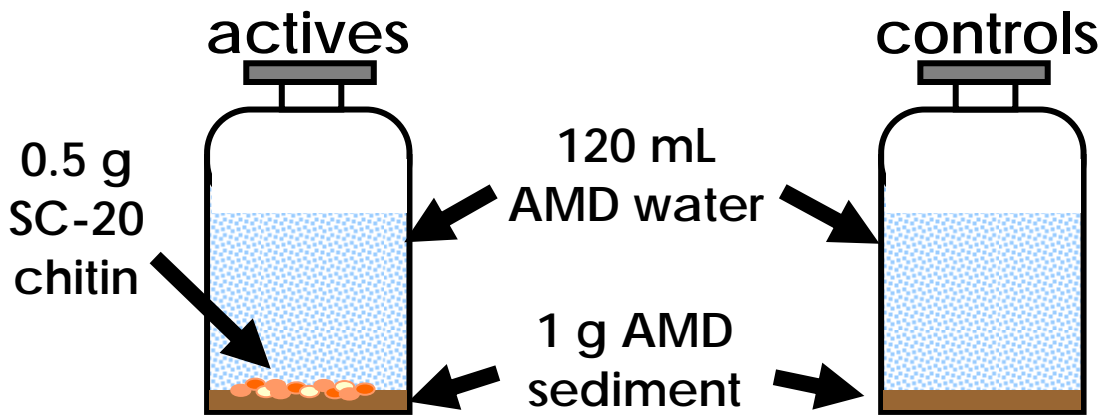


Figure 4. Schematic of the microcosm experiments.



Figure 5. Photograph of continuous flow columns in the laboratory to test the effectiveness and longevity of chitin for the remediation of acid mine drainage.