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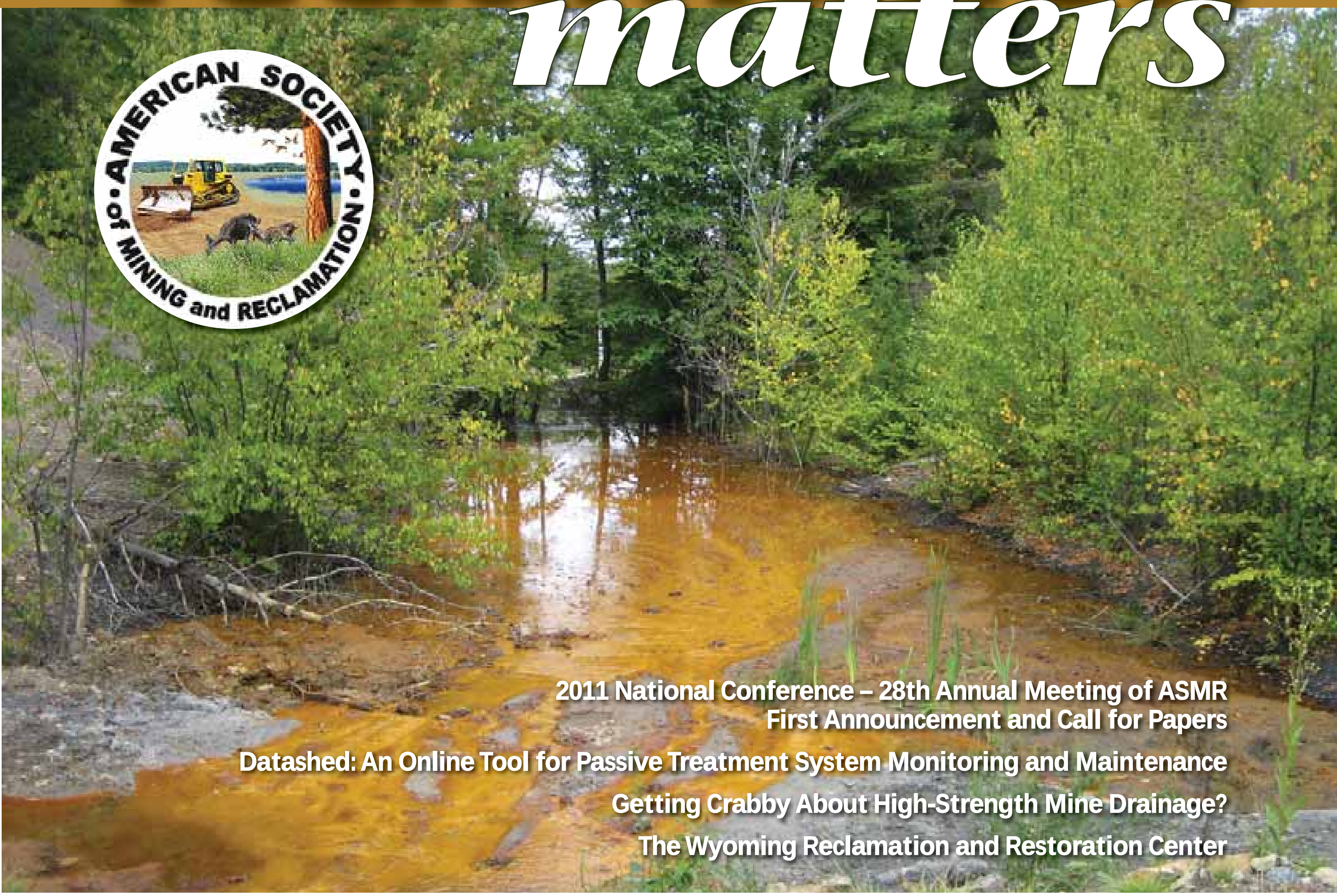

2011 National Conference – 28th Annual Meeting of ASMR
First Announcement and Call for Papers

Datashed: An Online Tool for Passive Treatment System Monitoring and Maintenance

Getting Crabby About High-Strength Mine Drainage?

The Wyoming Reclamation and Restoration Center

Getting Crabby about High-Strength Mine Drainage?

The combination of chitin, protein, and calcium carbonate in crab shells may offer a passive treatment solution

By Rachel Brennan, Penn State University

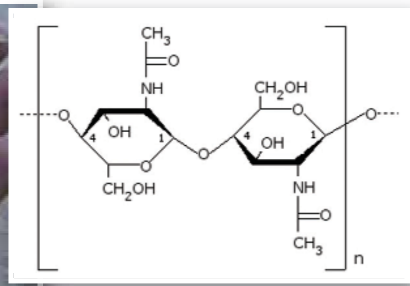

Figure 1: From left to right: a Dungeness crab, one of the main sources of commercially available chitin; a handful of processed crab shell particles used in remediation projects; and the chemical structure of two chitin monomers (N-acetylglucosame, NAG) connected by a □-1,4-linkage.

The bad news: funding cuts expected for passive treatment systems. The new *AMD Set-Aside Program Implementation Guidelines* established by the Pennsylvania Department of Environmental Protection (PA DEP) in 2009 warn against the use of state grant money to implement passive systems for treating "high risk" AMD. They define high risk on a sliding scale based on metals concentration and flow rate, but it can be generally described as net acidic water with a combined metals (Fe + Al) concentration of greater than 50 mg/L. This restriction in funds for AMD remediation projects is understandable: High levels of metals loading often leads to premature clogging of the treatment substrate with metal hydroxide precipitates, essentially rendering the systems useless in a relatively short period of time. Our research, however, indicates that high-strength AMD can indeed be treated with proper design and substrate selection.

The good news: multifunctional substrates. Since 2005, we have been experimenting with using crab shells as an alternative substrate for AMD treatment (Figure 1). Crab shells are a sustainable and commercially-available waste product of the shellfish industry, composed of a complex matrix of chitin, protein, and calcium carbonate ($CaCO_3$). This unique combination has been shown to biologically reduce sulfate, chemically enhance alkalinity, and physically remove metals from mine impacted water (MIW) at the bench scale (Daubert and Brennan, 2007; Robinson-Lora and Brennan, 2009; Robinson-Lora and Brennan, 2010a; Newcombe and Brennan, 2010) and in field trials (Venot et al. 2008) without the addition of limestone. The secret? The crab shell contains a high percentage (~40 percent by weight) of biogenic calcite with a high surface area. The micro-porous structure of crab shells provides a surface area that exceeds that of powdered limestone, thereby enabling high neutralization capacity and the complete removal of metals as hydr(oxides) and carbonates under continuous-flow conditions (Robinson-Lora, 2009). The release of phosphates and organic compounds also work to increase the alkalinity of water in crab-shell treated systems. Of special significance is the ability of crab shells to induce the removal of manganese, a particularly recalcitrant metal in AMD, even under field conditions at circum-neutral pH (Venot et al. 2008). It has also been shown that the chitin, and to a lesser extent the protein, in crab shells can remove some of the metals in AMD through biosorption (Robinson-Lora and Brennan, 2010b).

Table 1 (below): Water quality characteristics of the Klondike-1 discharge.
Figure 2 (right): Acid mine drainage seeps from abandoned coal mine tailings at the Klondike-1 site.

Parameter	Value
Hot acidity (mg/L as $CaCO_3$)	285
Alkalinity (mg/L as $CaCO_3$)	0
Design flow, maximum (gpm)	42
Typical flow, average (gpm)	15
Total Iron (mg/L)	93.2
Aluminum (mg/L)	4.5
Manganese (mg/L)	24.9
pH	3.9
Sulfate (mg/L)	692

Proof-of-concept research. In our initial work, we used crab shell as a sole substrate for enhancing AMD treatment. In batch tests with moderately strong AMD from a former bituminous coal mining area, crab shell increased the pH from 3.21 to 6.79, raised the alkalinity from 0 to 235 mg/L as $CaCO_3$, reduced dissolved Fe and Al concentrations by over 99 percent, and reduced Mn by 81 percent in just nine days (Daubert and Brennan, 2007). Subsequent testing has yielded even greater contaminant reductions. In columns with a hydraulic retention time of 11.2 h, 25 g of crab-shell chitin was able to completely remove Fe, Mn, and Al for 174, 234, and >268 pore volumes, respectively, while continuously supplying alkalinity at a rate of 50 mg $CaCO_3$/day (Robinson-Lora and Brennan, 2009).

So, how much does it cost? While the multifaceted capabilities of crab shell make it attractive for use in passive remediation systems, economic considerations are also important. Unrefined crab shell is a relatively inexpensive microbial substrate, retailing at $1.32/kg ($0.60/lb), but it is expensive in comparison to spent mushroom compost (SMC), which costs only $0.055/kg ($0.025/lb). We have demonstrated, however, that SMC is not as effective as crab shell for the removal of many metals, especially manganese (Robinson-Lora and Brennan, 2010a), which minimizes the importance of the initial capital cost savings it offers. A true economic benefit may be realized by adding fractional amounts of crab shell to SMC in order to improve the efficiency of the substrate with little, if any, added cost over traditional systems. By increasing the efficiency of the substrate, it should be possible to reduce the overall size and cost of passive AMD treatment systems.

Substrate mixtures may be best To evaluate different crab-shell/SMC mixtures for their ability to neutralize acidity, reduce sulfate, and remove metals in field-collected AMD, batch and continuous-flow column tests were conducted. Alkalinity generation and the removal of manganese and sulfate were strongly correlated to the fraction of crab shell in the substrate: The treatment capacity increased from 36.7 L/kg for the traditional 90 percent SMC/10 percent limestone substrate up to 428 L/kg for 100 percent crab shell (Newcombe and Brennan, 2010). The costs associated with adding crab shell to SMC were found to be minimal relative to the resulting improvement in water quality. Based on these data, it appears that a small fraction of crab shell (5 to 15 percent) does not provide a significant benefit over traditional compost and limestone substrates, but that larger fractions (50 to 100 percent) are more efficient than traditional SMC substrates, especially for the removal of metals. By adding fractional amounts of crab shell to SMC, treatment capacity and efficiency are improved, thus allowing for a smaller treatment system to remediate equivalent volumes of AMD.

Throwing down the gauntlet: finding a "high risk" discharge for a field demonstration. Over the past several years, we have been looking for a high risk discharge on which to test our crab shell mixtures at the field scale. After carefully considering the need for treatment, site accessibility, and level of cooperation of the local watershed groups, the site for our field demonstration was selected: the abandoned Klondike Mine in Cambria County, PA (Table 1, Figure 2). The U.S. EPA and other organizations have determined that restoration of this site is imperative to the health

Figure 3. Dr. Brennan and the continuous-flow column system that her research group uses to test different substrate combinations for the treatment of high-strength acid mine drainage. PHOTO CREDIT: SARA BRENNEN.

of downstream receiving waters in the Clearfield Creek Watershed and, as a result, have awarded in excess of $600,000 in grants toward its remediation. These funds have supported the design and construction of two nearly-identical treatment systems to treat the two discharges: Klondike-1 (KL-1) to treat discharge 32-R2 (93 mg/L Fe, 15 gal/min) and Klondike-2 (KL-2) to treat discharge 32-R2A (5 mg/L Fe, 166 gal/min). Although a series of large oxidation and vertical flow ponds are successfully cleaning the less-contaminated KL-2 discharge, the spatially restricted, smaller treatment system for KL-1 is removing only about 75 percent of the Fe and acidity. It is believed that the deficiency of the KL-1 treatment system is due in part to high concentrations of ferric iron (Fe^{3+}) clogging the SMC substrate in the vertical flow pond. In short, the KL-1 system was under-designed for the substrate selected and level of contamination present.

Restoration of the KL-1 site, and treatment of other similar discharges, presents a practical and intellectual challenge: How can we achieve a higher degree of treatment within a pre-existing small footprint? We believe the answer is through proper design and substrate selection. In side-by-side field tests with AMD from a former hard-rock mine in Colorado, crab shell has not clogged while other substrates have (Venot et al. 2008). We theorize that the non-clogging nature of crab shell is due to its ability to maintain low redox conditions, which keeps iron in a reduced, soluble state (ferrous iron, Fe^{2+}), allowing it to pass through the substrate without precipitating. Nevertheless, the application of crab shell substrates to high-strength water had not yet been tested, so during the past year, we evaluated different substrate combinations and retention times for treating the KL-1 discharge. Using a series of continuous-flow column tests (Figure 3), we observed that substrates containing 70 percent chitin by mass mixed with SMC offer the best balance of treatment effectiveness and cost, but that 100 percent chitin offers the greatest longevity (Grembi et al. 2010). With support from the National Science Foundation, the Foundation for Pennsylvania Watersheds, and the Clearfield Creek Watershed Association, a field demonstration of these substrates compared to the original SMC/limestone mixture used at the site is underway.

Pilot test design. The pilot field test at the KL-1 site consists of four replicate reactors (1,000-gallon plastic septic tanks, Figure 4) containing the following substrate mixtures: the original 90 percent SMC/10 percent limestone mixture currently used at the KL-1 site (negative control); 70 percent crab shell mixed with 30 percent SMC (Figure 5); and 100 percent crab shell (positive control). All of these substrates were placed over a limestone underdrain. An additional 70 percent crab shell/30 percent SMC reactor was constructed with a sandstone underdrain to see if the crab shell could provide enough alkalinity that the limestone underdrain could be omitted and costs reduced in future applications. A portion of the flow from the current primary oxidation/settling pond at KL-1 was diverted through a buried PVC-pipe network (Figure 6) and split into these four reactors to give a hydraulic residence time of ~16 hours. Aeration of the effluent water via cascades and aeration ponds (Figure 7) should allow Fe^{2+} to oxidize and precipitate out as Fe^{3+}, and simultaneously strip out residual ammonia that may be released from the crab shell at early times (Korte et al. 2008). Water sampling and analysis of the influent and effluent from the reactors will be conducted weekly for the first month, biweekly for the next month, and then monthly for the remainder of the year to determine the effects of the substrates on water quality. In addition, DNA and RNA samples (Figure 8) will be taken from the different reactors at these sampling times to examine the relationship between microbial community development and water quality, so that future optimization of passive systems for the treatment of high risk AMD may be enabled. This is the first pilot test of this technology for treating high-strength AMD at the field scale and is a necessary step toward validating the technology for full-scale application.

Future plans. Water quality analyses taken over the next year will help determine if a full-scale retrofit of the KL-1 site is warranted. This project is being supported in part by a multiyear grant from the National Science Foundation (CAREER Award CBET-0644983), which continues through 2012. If this pilot test is successful, then full-scale restoration of the KL-1 site will be initiated with partial support of this NSF grant. Dr. Brennan's design classes (Figure 9), research team, and the Clearfield Creek Watershed Association will monitor the system for as long as funding permits, and will seek new funds to continue evaluating the effectiveness of the system into the future. Fundamentally, the results of this project should provide insights into innovative passive treatment methods that can be used for remediating high risk AMD within small treatment footprints.

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Figure 4. Penn State Environmental Engineering graduate student, Jessica Grembi, guides one of the pilot reactors into position at the Klondike-1 site.

Figure 5. President of the Clearfield Creek Watershed Association, Earl Smithmeyer, and Penn State undergraduate Honors student, Sara Goots, add a mixture of crab shells and spent mushroom compost into one of the pilot reactors.

Figure 6. Influent to each of the reactors is provided through individual pipelines from the current primary oxidation/settling pond on site. After installation, the pipes were buried to prevent freezing in winter.

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Figure 7. Effluent from each reactor will cascade into a series of two aeration/settling ponds, and then be piped to the existing aerobic wetland on site.

Figure 8. Permeable substrate bags inserted into the pilot reactors for later microbial community analysis, arranged left to right: spent mushroom compost and limestone chips, crab shell and spent mushroom compost, and crab shell only.

Figure 9. Penn State Civil Engineering undergraduates Brad Sick, Gary Warren, and MacKenzie Muryn take water quality measurements at the Klondike site for their CE497B class. The course, Field Methods for Remediation Design, is taught by Dr. Brennan with the support of a Faculty Early Career Development (CAREER) award from the National Science Foundation.