

# REMEDICATION OF HIGH-STRENGTH MINE INFLUENCED WATER WITH CRAB SHELL SUBSTRATE MIXTURES: LABORATORY COLUMN AND FIELD PILOT TESTS<sup>1</sup>

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**Abstract:** Anaerobic passive treatment systems remediating high-strength mine influenced water (MIW) have failed to consistently treat sources with high metals loads and flow rates. For example, the high iron (140 mg/L) and acidity (390 mg/L as CaCO<sub>3</sub>) of the Klondike-1 discharge near Ashville, PA, caused premature clogging of a vertical flow pond which was filled with a limestone buffered organic substrate (90% spent mushroom compost (SMC) and 10% limestone chips). In this study, continuous-flow columns and pilot-scale field reactors were used to evaluate if treatment of high-strength MIW can be improved using crab shell as a substrate amendment.

For the lab study, eight columns were wet-packed with substrate mixtures ranging from 0 – 100% crab shell (with the balance SMC), and fed Klondike-1 water to produce a 16 hr hydraulic residence time (HRT). After determining the best performing substrate mixture in the column test, a pilot-scale field study was initiated in August 2010, in which 1,000 gallon (3,785 L) tanks were filled with a limestone underdrain and an upper substrate layer of: 1) 100% crab shell; 2) 70% crab shell + 30% SMC; or 3) 90% SMC + 10% limestone. A fourth tank containing a sandstone underdrain with a 70% crab shell + 30% SMC substrate layer was installed to determine if similar performance could be achieved without the limestone underdrain. All columns and field reactors also contained sand as a proppant to ensure hydraulic conductivity. Aqueous samples were collected from the columns/reactors over time and analyzed for pH, ammonium, acidity, alkalinity, DOC, anions, and metals. In the column study, an optimum ratio of 70% crab shell + 30% SMC sustained complete iron removal, pH above 5.0, and excess alkalinity generation for twice as long as the traditional SMC and limestone substrate. To date, the field study is still achieving complete iron removal, and other results generally mirror the laboratory findings.

**Additional Key Words:** anaerobic passive treatment, metals removal, alkalinity generation

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## Introduction

The Clearfield Creek Watershed Association (CCWA) is a volunteer group dedicated to the improvement and maintenance of high quality water and biota within the watershed of the Clearfield Creek, whose waters eventually flow into the Chesapeake Bay. Acidic discharges from the abandoned Klondike mine, located near Ashville, Pennsylvania, have contributed to the impairment of the Little Laurel Run, a tributary of Clearfield Creek. Two discrete discharges were identified at the Klondike site and funds were obtained by the CCWA to design and build a treatment system for each discharge. Monitoring of the Klondike-1 discharge indicated an average Fe concentration of 141 mg/L, acidity of 390 mg/L as CaCO<sub>3</sub>, Mn of 30 mg/L, Al of 2.8 mg/L, pH 3.3, and flow rate of 57 L per minute (Rose, 2008). Average SO<sub>4</sub><sup>2-</sup> for this discharge is 963 mg/L.

Typically, the most cost-effective method to remediate mine influenced water (MIW) is passive treatment, and the only systems capable of removing all components (metals, sulfur species, and acidity) of MIW are anaerobic biological passive treatment systems, which utilize sulfate reducing bacteria (SRB) to facilitate the precipitation of metal sulfides while simultaneously generating alkalinity. Vertical flow ponds (VFPs) are one approach to anaerobic passive treatment which allows water to flow vertically downward through an anoxic layer of a limestone buffered organic substrate, and then through a layer of limestone rock to produce additional alkalinity before exiting through a network of underdrains (**Error! Reference source not found.**). These system designs typically include an additional treatment cell subsequent to the VFP in the form of a setting pond where aeration is encouraged and additional metal (hydr)oxides precipitate from the neutralized water.

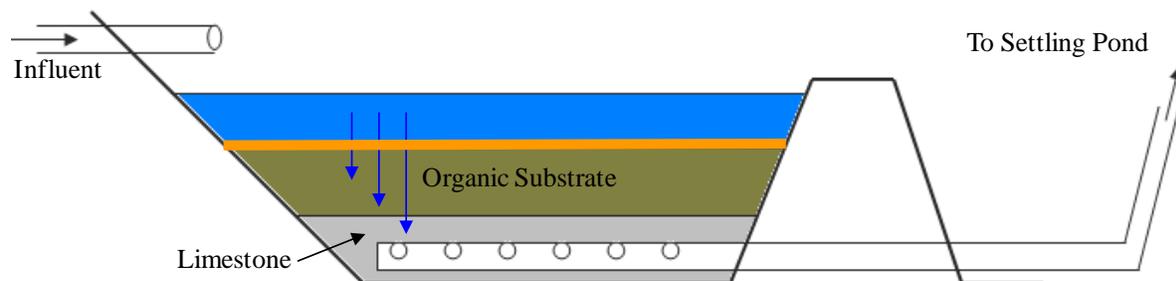


Figure 1. Cross-sectional schematic of a vertical flow pond (VFP).

The treatment system designed for the Klondike-1 discharge consisted of a primary oxidation pond, VFP, an aerobic settling pond, and then a constructed wetland as a final polishing step. The VFP contained a limestone buffered organic substrate (LBOS) which was comprised of 90% spent mushroom compost (SMC) + 10% limestone chips). The VFP design was based on an estimated 25 yr life for the limestone and 35 g of acidity (as  $\text{CaCO}_3$ )/day/m<sup>2</sup>, which resulted in surface dimensions for the pond of 78 ft by 125 ft (24 m by 38 m). The limestone underdrain layer was 2 ft (60 cm) deep, overlain with a one ft (30 cm) layer of LBOS, and a standing water depth on top of the substrate of 5 ft (150 cm) (Rose, 2008). Construction was completed in November 2007, but within 9 months the VFP had clogged due to a layer of Fe precipitates which formed on top of the organic substrate layer (orange layer in **Figure 1**). The main cause of the excess precipitation was likely a combination of three factors: 1) the system was designed based on the average rather than maximum flow rate; 2) the primary settling pond was the proper volume to theoretically meet the recommended HRT, but its excessive depth of 8 ft (2.4 m) and shape of 55 by 85 ft (17 by 26 m) may have resulted in short-circuiting and limited the extent of oxidation and precipitation; and 3) the standing water on top of the VFP is 2-3 ft (61-91 cm) deeper than recommended, thus increasing HRT of the water on top of the substrate, and potentially promoting unwanted precipitation in this location. The Fe precipitates were removed from the VFP and two additional oxidation ponds were constructed at the beginning of the treatment system to facilitate additional low-pH Fe oxidation. However, the system has the potential to clog again if these cells do not operate as designed. In addition, even in optimal operating conditions the system was unable to sufficiently remove manganese from the water, and thus was unable to completely neutralize acidity.

Research investigating crab shell, which contains carbon, nitrogen, and alkalinity in a complex matrix of chitin, protein, and  $\text{CaCO}_3$ , has shown simultaneous biological, chemical, and physical remediation of low-strength MIW (Robinson-Lora and Brennan, 2009; Robinson-Lora and Brennan, 2010; Newcombe and Brennan, 2010). In previous laboratory and field studies, crab shell has out-performed other substrates by rapidly removing iron and aluminum, as well as manganese, something which other substrates have been unable to accomplish at circumneutral pH. These results led to the suggestion that crab shell could be utilized at the Klondike-1 site as a substrate amendment within the VFP to simultaneously remove Mn and also achieve complete neutralization within the given small footprint.

In this study, continuous-flow columns were used to evaluate if treatment of high-strength MIW from the Klondike-1 discharge could be improved using crab shell as a substrate amendment, thus providing a more reliable alternative to the traditional substrates which have not displayed consistent performance. Once confirmed with laboratory data, field-scale pilot systems were established at the Klondike-1 site and are currently in operation to treat a portion of the flow from that discharge.

## **Materials and Methods**

### **Water Source**

All water used for the continuous-flow column test was collected from the Klondike-1 site. Water was collected approximately 750 ft (230 m) downstream from the point of emergence from a non-stagnant, deep channel section of the discharge stream. Flexible plastic tubing (1-in/2.5 cm diameter) and a hand pump were used to transfer the water into high-density polyethylene containers, which were capped with minimal headspace. Water was collected from the location described above five times throughout the duration of the continuous-flow test. Water for the pilot test is diverted from the final oxidation pond immediately preceding flow into the VFP.

### **Continuous-Flow Column Setup**

Continuous-flow columns were used to simulate the flow through a VFP containing different substrates. Columns were constructed using 2 ft (61 cm) long, 1.5 in (38 mm) diameter PVC pipe (Harvel Clear™ Schedule 40 PVC pipe and fittings, United States Plastic Corp.) with end-caps of the same material (**Figure 2**). Columns were flushed with Argon gas during packing to remove oxygen and allow for anoxic packing conditions. Solids were wet-packed into the column in approximately one inch (2.5 cm) lifts with free-standing source water, beginning with 30 g of sand (to prevent loss of substrate through influent port). Each column was packed with a total of 40-g of substrate mixed with a sand proppant to fill the majority of the column (~700 mL) while maintaining hydraulic conductivity. A second sand plug was added to the effluent end of the column to completely fill the remaining volume and aid in preventing substrate particles from flowing out of the system. A second end cap was then cemented on the top of each column.

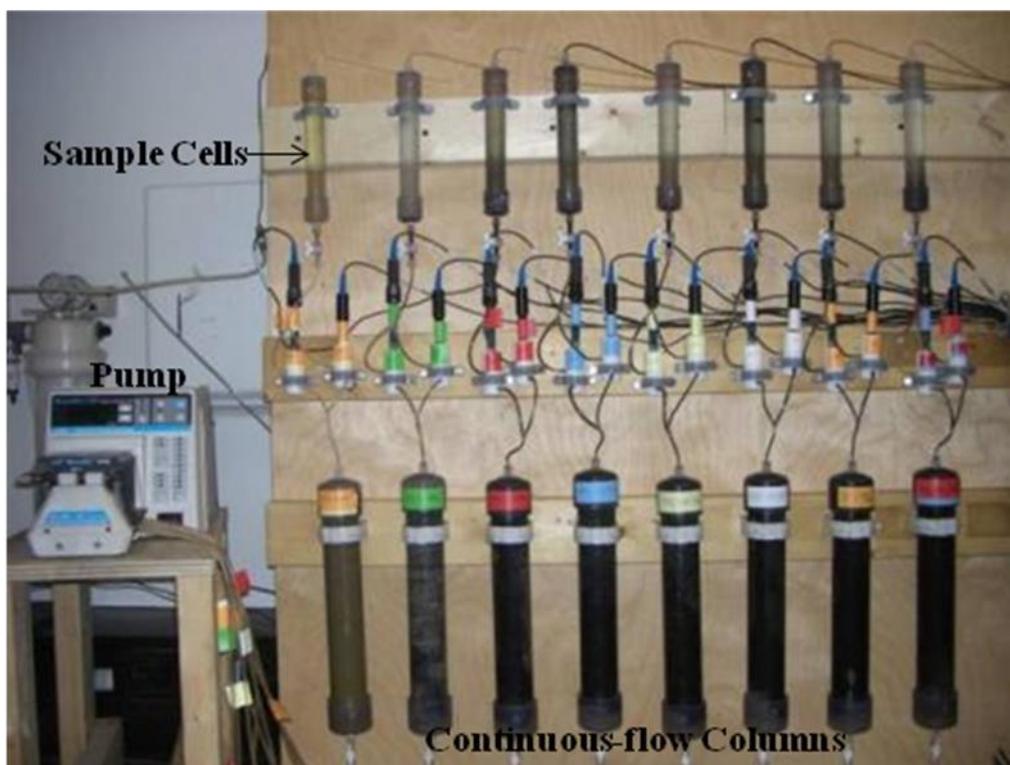


Figure 2. Laboratory continuous-flow columns used to treat Klondike-1 MIW.

The following substrates were used to promote the remediation of the collected water in the laboratory column tests: ChitoRem® Chitin Complex (grade SC-20, JRW Bioremediation, Lenexa, KS); SMC (Mushroom Test Demonstration Facility, The Pennsylvania State University); and limestone (0.420-0.841mm, 88.89%  $\text{CaCO}_3$ , New Enterprise Stone and Lime Company, Tyrone, PA). The ChitoRem® Chitin Complex, subsequently referred to as crab shell (CS), is a product derived from Dungeness crab shell and contains ~10% chitin, ~12% protein, and ~78% mineral matter (62% as  $\text{CaCO}_3$ ) (Robison-Lora and Brennan, 2009).

Based on previous column studies and microcosm experiments (Newcombe and Brennan, 2010), incremental fractions of crab shell between 50% and 100% (by mass) were mixed with SMC (**Table 1**) and then further mixed with various amounts of sand proppant. A 100% sand column was used as an experimental control, and a column filled with the traditional 90% SMC and 10% limestone substrate was also used for comparison purposes. Columns were provided an 8-day incubation period after packing to promote establishment of the indigenous microbial community, prior to the initiation of continuous-flow conditions.

Table 1. Mass of solid packing materials used in each continuous-flow column.

Column Name	Column Contents (g)			
	Crab Shell (CS)	SMC	Limestone (LS)	*Sand
<b>Sand Control</b>	0	0	0	666
<b>100% CS</b>	40	0	0	475
<b>90% CS/10%SMC</b>	36	4	0	431
<b>80% CS/20%SMC</b>	32	8	0	465
<b>70% CS/30%SMC</b>	28	12	0	412
<b>60% CS/40%SMC</b>	24	16	0	507
<b>50% CS/50%SMC</b>	20	20	0	459
<b>Traditional</b>				
<b>90%SMC/10% LS</b>	0	36	4	545

\*Includes bottom plug + amount mixed as a proppant with substrate + top plug

Source water was pumped from a 50-L reservoir vertically upward through each column by a peristaltic pump consisting of a digital drive and 4-roller cartridge head (Masterflex L/S, Cole-Parmer) at a set rate of 0.25 mL/min to produce a 16-hr HRT. Although VFPs utilize a down-flow, the up-flow configuration was used during the experiment to provide a consistent flow through each column and prevent short-circuiting. All water storage containers were continuously purged with argon gas to maintain an anoxic environment and reduce iron oxidation. In addition, the influent water reservoir and the columns were covered with opaque black plastic for the duration of the test to prevent the growth of phototrophic organisms.

Sampling cells 7.5 in (19.1 cm) in length were constructed from ¾ in (19.1 mm) diameter PVC (Harvel Clear™ Schedule 40 PVC pipe and fittings, United States Plastic Corp.) and placed at the effluent end of the columns to facilitate sample collection for analysis (**Figure 2**). Effluent was routed from the sampling cell into an open-topped bin to simulate an aerobic settling pond with a 45-hr HRT, which is typically used following VFPs to oxidize and remove metals. The simulated aerobic settling pond drained into a second sampling cell, identical to the first.

Columns were sampled every 1-7 days during continuous-flow conditions, depending on the observed rate of changes in water quality. Samples collected from the first sampling cells (before the aerobic settling pond) were measured immediately for pH, ORP, acidity, alkalinity, and ammonium and a sample was preserved for later analysis of dissolved metals. Samples were concurrently collected from the second sampling cells and preserved for dissolved metals analysis.

## Field Pilot System Setup

The pilot system included four treatments which each consisted of a 1,000 gal (3,785 L) tank reactor (dimensions of roughly 2.5 m long by 1.5 m wide by 1.4 m tall) fitted with an underdrain piping network (to simulate a VFP) and two subsequent 300 gal (1,135 L) aerobic settling ponds arranged in series. The piping network consisted of a main pipe running down the center of the reactor with five perpendicular branches extending at roughly 18 in (46 cm) intervals. The pilot-VFPs were filled with a rock/underdrain layer, a substrate layer (including sand proppant) and an upper layer of pea gravel to hold down the substrate as the density of crab shell (0.45 g/mL) is less than water (Figure 3). Three of the reactors contained a limestone underdrain and an upper substrate layer of: 1) 100% crab shell; 2) 70% crab shell + 30% SMC; or 3) 90% SMC + 10% limestone. A fourth reactor containing a sandstone underdrain with a 70% crab shell + 30% SMC substrate layer was installed to determine if similar performance could be achieved without the limestone underdrain.

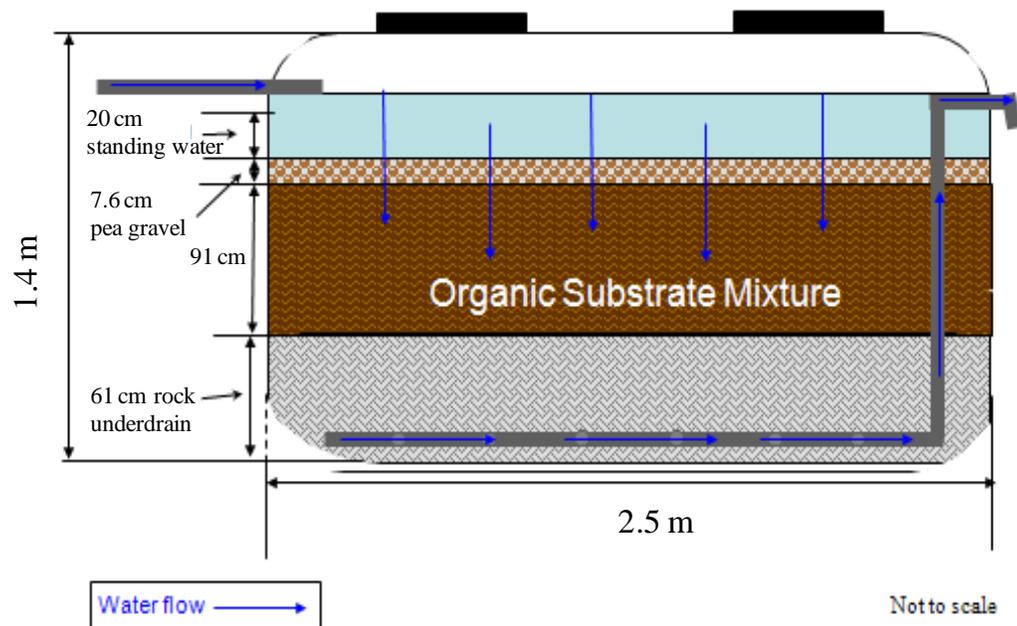


Figure 3. Schematic of pilot-scale VFPs installed at Klondike-1 field site.

The organic substrate layer of the reactors consisted of various mixtures (**Table 2**) of the following: crab shell; SMC (available onsite from the construction of the previously installed treatment system); white silica sand (Seymore Brothers, Inc., Altoona, PA), limestone chips (91%  $\text{CaCO}_3$ , available onsite from the construction of the previously installed treatment system),

and pea gravel (Somogyi’s Route 22 Supply, Ebensburg, PA). The underdrains were constructed approximately 2 ft (61 cm) deep with 3 in (7.6 cm) rocks: limestone rock (AASHTO#1, 99.3% CaCO<sub>3</sub>, New Enterprise Stone and Lime Company, Tyrone, PA), sandstone rock (#4 Sandstone, 0% CaCO<sub>3</sub>, Kinkead Aggregates, Homer City, PA).

Table 2. Mass of organic substrate layer, and CaCO<sub>3</sub> equivalents for the substrate and underdrain layers in each pilot-scale VFP.

Reactor	Reactor Organic Substrate Layer Components (kg)				CaCO <sub>3</sub> equivalents (kg as CaCO <sub>3</sub> )		
	Crab Shell (CS)	Sand	SMC	LS chips	Substrate Layer	Underdrain Layer	Total
<b>100% CS + LS Underdrain</b>	685	685	0	0	185	2400	2590
<b>70% CS/ 30% SMC + LS Underdrain</b>	577	576	247	0	173	2400	2570
<b>70% CS/ 30% SMC + SS Underdrain</b>	577	576	247	0	173	0	173
<b>90% SMC/ 10% LS + LS Underdrain</b>	0	0	549	61	93	2400	2490

Water was piped individually into each pilot-VFP at a flow rate of 0.2 gal/min (0.76 L/min, regulated by an orifice), flowed vertically downward through the substrate (design HRT of 17.5 hr) and exited through the underdrain system onto a corrugated plastic cascade which was designed to increase aeration before water reached the first settling pond (**Figure 4**). Water flowed from the first into the second settling pond and then exited the system via a piping network which discharged into the constructed wetland of the previously installed treatment system at the site.

Reactors were sampled every week for the first month (September 2010), biweekly for another month and then monthly thereafter for a minimum of one year. Field probes were used onsite to measure pH, ORP, conductivity, and temperature of the reactor effluent and of the final aerobic settling pond. Samples were collected from the reactor effluent, transported on ice to the laboratory and measured within 4 hours for pH, acidity, alkalinity, and ammonium, and a sample was preserved for later analysis of dissolved metals, anions, and DOC. Samples were concurrently collected from the second aerobic settling pond and preserved for dissolved metals analysis.



Figure 4. Pilot-scale VFPs and subsequent aerobic settling ponds installed to treat MIW at the Klondike-1 field site. Photo taken on April 26, 2011, by Brandon Diehl, Foundation for Pennsylvania Watersheds.

#### Analytical Methods

The pH was measured on the extracted samples using a bench-top electrode (Thermo-ORION) connected to a pH/mV meter (Accumet® Basic AB15, Fisher Scientific). Ammonium was also measured using an electrode (ISE ORION 9512) and the same pH/mV meter, and compared to 1 mg/L and 10 mg/L ammonium standards. Acidity and alkalinity were measured using titrations as described in *Standard Methods for the Examination of Water and Wastewater* (Methods 2310 and 2320; APHA 1998). Endpoints used for these titrations were pH 4.5 for alkalinity and pH 8.3 for acidity. pH, ammonium, acidity, and alkalinity were all measured within 4 hours of sample collection. Samples were prepared for dissolved metals analysis by filtering with a 0.45 $\mu$ m filter, acidifying to pH < 2 with 60-70% HNO<sub>3</sub>, and sparging with lab air through a 25 gauge needle for 5 minutes (to drive off hydrogen sulfide). These samples were sent to the Pennsylvania State University Materials Characterization Laboratory to be measured using inductively coupled plasma-atomic emission spectrometry (ICP-AEP; Leeman Labs PS300UV). ORP was measured in the field using an Oakton® Waterproof ORPTestr 10 and temperature, pH, and conductivity were measured using an Oakton® Multi-Parameter Tester 35.

## Results

### Continuous-Flow Column Experiment

pH, Alkalinity, and Acidity. All treatment columns increased the pH from influent values (average pH 2.54) to above 6.0. Columns containing any fraction of crab shell maintained pH above 6.0 longer than the traditional substrate (90% SMC + 10% LS), which was only able to sustain this treatment for 48 days (55 PV). The 100%, 90%, and 70% crab shell columns all maintained pH above 6.0 for nearly twice as long as the traditional substrate (**Table 3**).

Table 3. pH values and alkalinity generation longevity achieved in continuous-flow columns treating Klondike-1 MIW.

Treatment Column	Max. pH	pH sustained above 6.0		pH returned to influent value		Net alkaline effluent		Alkalinity generation exhausted	
		(days)	(PV)	(days)	(PV)	(days)	(PV)	(days)	(PV)
<b>Sand Control</b>	2.64	0	0	0	0	0	0	0	0
<b>100% CS</b>	7.62	111	109	180+	176+	97	94	146	141
<b>90% CS/10%SMC</b>	7.26	90	98	180+	199+	90	98	132	150
<b>80% CS/20%SMC</b>	7.26	76	67	153	137	69	60	118	107
<b>70% CS/30%SMC</b>	7.16	90	96	180+	195+	90	96	133	147
<b>60% CS/40%SMC</b>	7.34	62	72	160	196	62	72	90	108
<b>50% CS/50%SMC</b>	7.15	76	87	132	161	69	80	103	123
<b>Traditional</b>									
<b>90%SMC/10% LS</b>	6.38	48	55	97	116	48	55	69	79

Sufficient alkalinity was generated in all treatments to completely neutralize the acidity present in the influent water (average hot acidity = 329 mg/L as CaCO<sub>3</sub>) from the onset of continuous-flow conditions. The column containing the traditional substrate mixture achieved a maximum alkalinity generation of 260 mg/L as CaCO<sub>3</sub> at the first sampling point following an eight day incubation period, whereas columns containing any fraction of crab shell substrate produced significantly higher alkalinity initially, with maximum values near 5,800 mg/L (90% crab shell column). Columns containing crab shell were able to maintain net alkaline conditions for longer than the traditional treatment substrate, nearly twice as long for the 100%, 90%, and 70% crab shell columns (Table 3. pH values and alkalinity generation longevity achieved in continuous-flow columns treating Klondike-1 MIW. Table 3).

Metals Removal. The primary metals of concern found in the Klondike-1 discharge are Fe and Mn. Dissolved metals were monitored at two locations: in the effluent of the continuous-flow column and also after the aerobic settling pond.

Results from the column effluent show that Fe (average influent value of 62.6 mg/L) was initially removed within the column substrate for all treatment columns. However, this trend is no longer consistent past 50-100 days in any of the columns. In comparison, Fe removal subsequent to aeration and precipitation in aerobic settling ponds was sustained significantly longer. Breakthrough (return to influent levels or higher) of dissolved Fe after the settling ponds occurred at approximately 140 days for the traditional substrate, and did not occur at all during the experiment (181 days) for the 100% crab shell column (Figure 5). The 70% crab shell column sustained almost complete removal until approximately 130 days and achieved partial removal throughout the remainder of the experiment.

Removal of dissolved Mn (average influent value of 36.1 mg/L) occurred over a much shorter time. The traditional substrate sustained dissolved Mn removal within the column for less than 10 days (11 PV) as compared to 27 days (32 PV) for the 70% crab shell column, and 62 days (56 PV) for the 100% crab shell column (Fig. 6). Dissolved Mn concentrations measured after aerobic settling were very similar to those measured in the column effluent, suggesting that contact with oxygen in the settling pond does not affect the removal of Mn.

#### Pilot-Scale Field Test

Pilot-scale field reactors were installed in August 2010 and have been in operation for approximately 120 days. However, due to freezing of the reactors during the winter months, only data for the first 90 days of the field monitoring is included below.

pH, Alkalinity, and Acidity. pH levels reached within the pilot system were slightly higher than those achieved in the continuous-flow columns. All four reactors have maintained pH above 6.5 for the 90 days of monitoring conducted thus far (Figure 6). Alkalinity generation within the traditional treatment reactor for the pilot system reached a maximum of 260 mg/L as CaCO<sub>3</sub> after incubation, identical to that achieved within this substrate during the continuous-flow experiment (Figure 7). In general, alkalinity and acidity from the field reactors are following the same trend as the continuous-flow columns, and all reactors are maintaining a consistent net alkaline effluent.

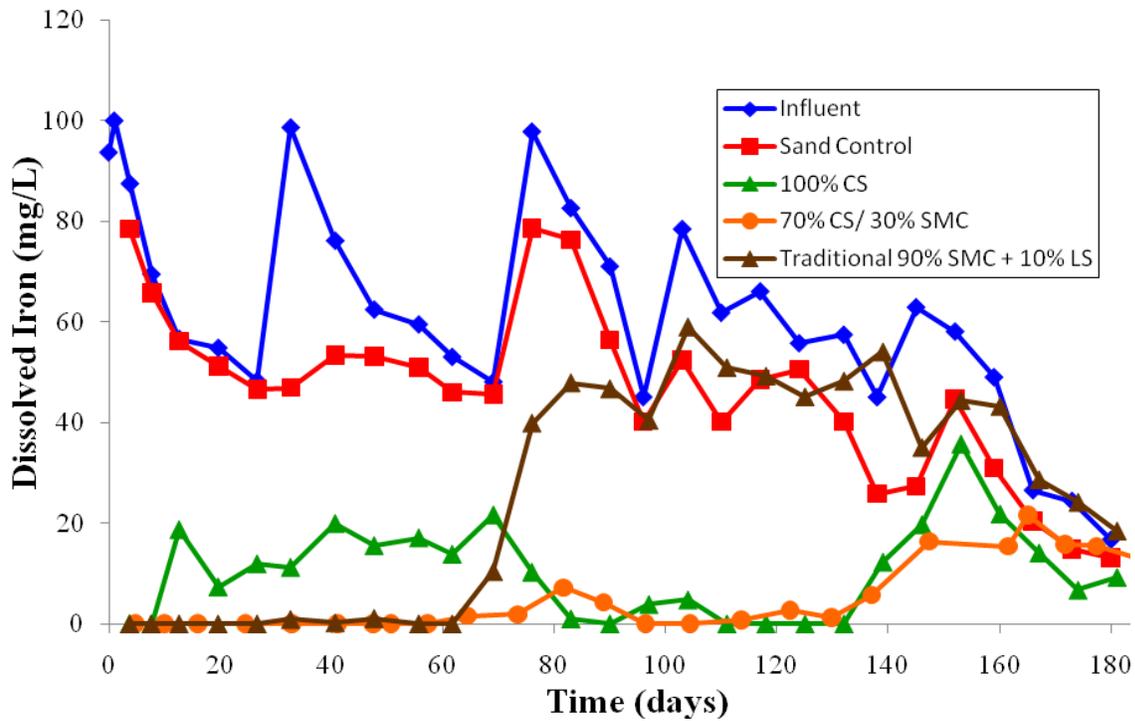


Figure 5. Dissolved iron measured after treatment of Klondike-1 MIW by different substrates in continuous-flow columns plus subsequent aeration and precipitation. Spikes in influent iron occurred immediately after fresh MIW was collected.

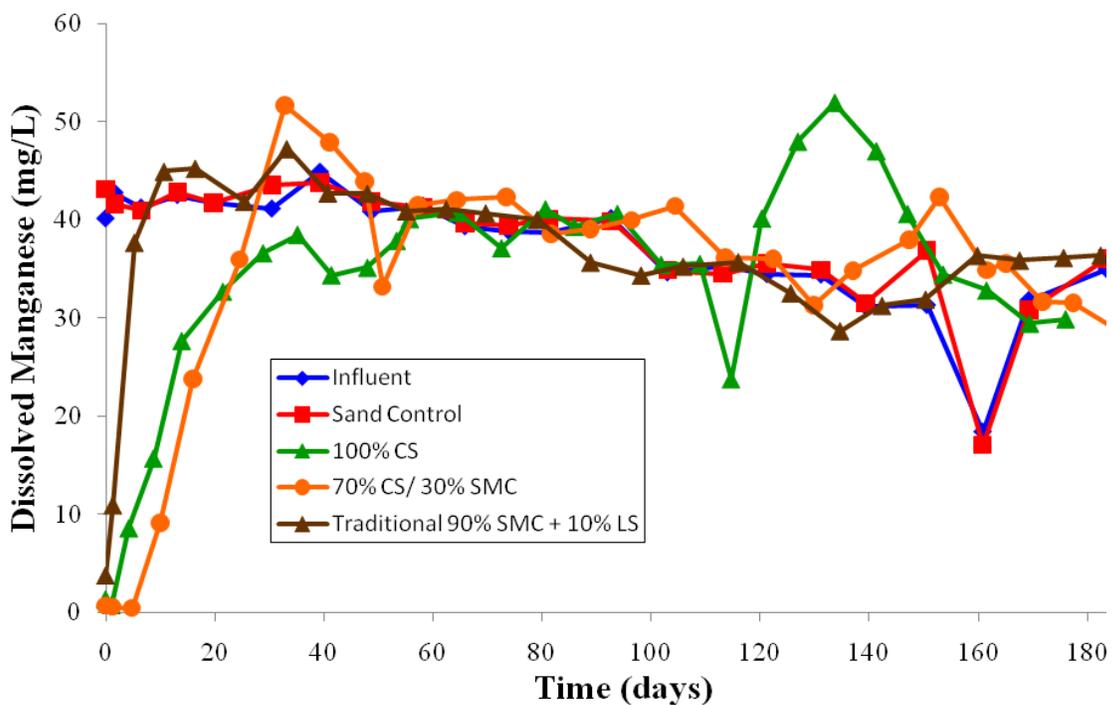


Figure 6. Dissolved manganese measured after treatment of Klondike-1 MIW by different substrates in continuous-flow columns.

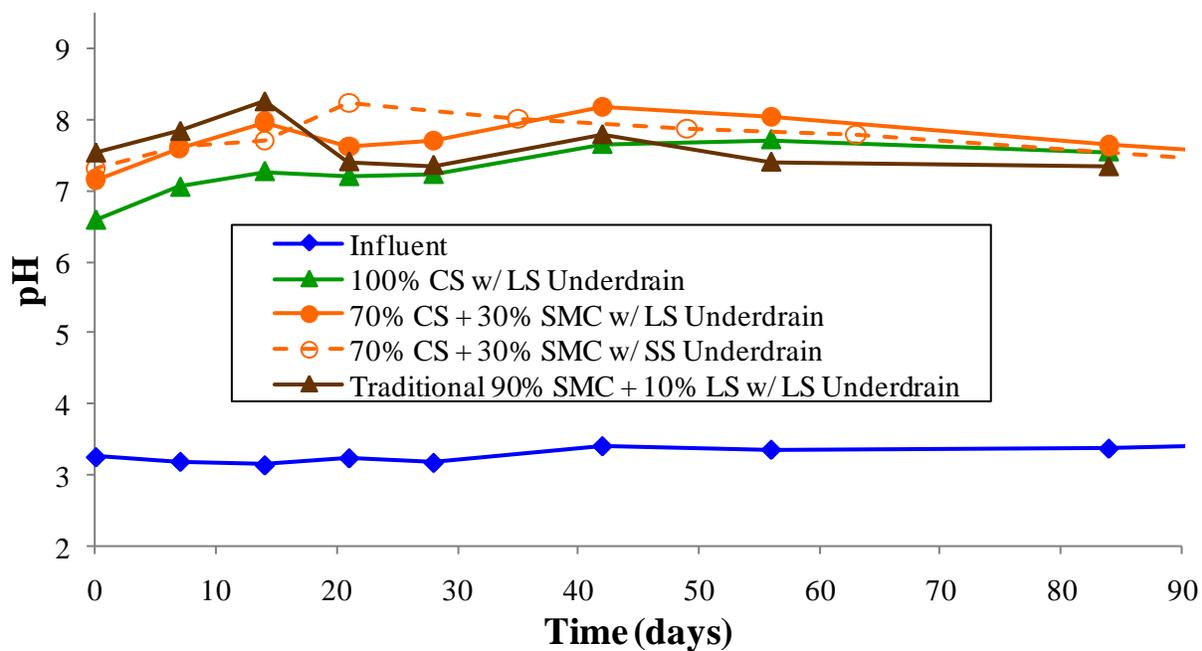


Figure 6. pH values of MIW influent and pilot-scale reactor effluent from initial 90 days of monitoring.

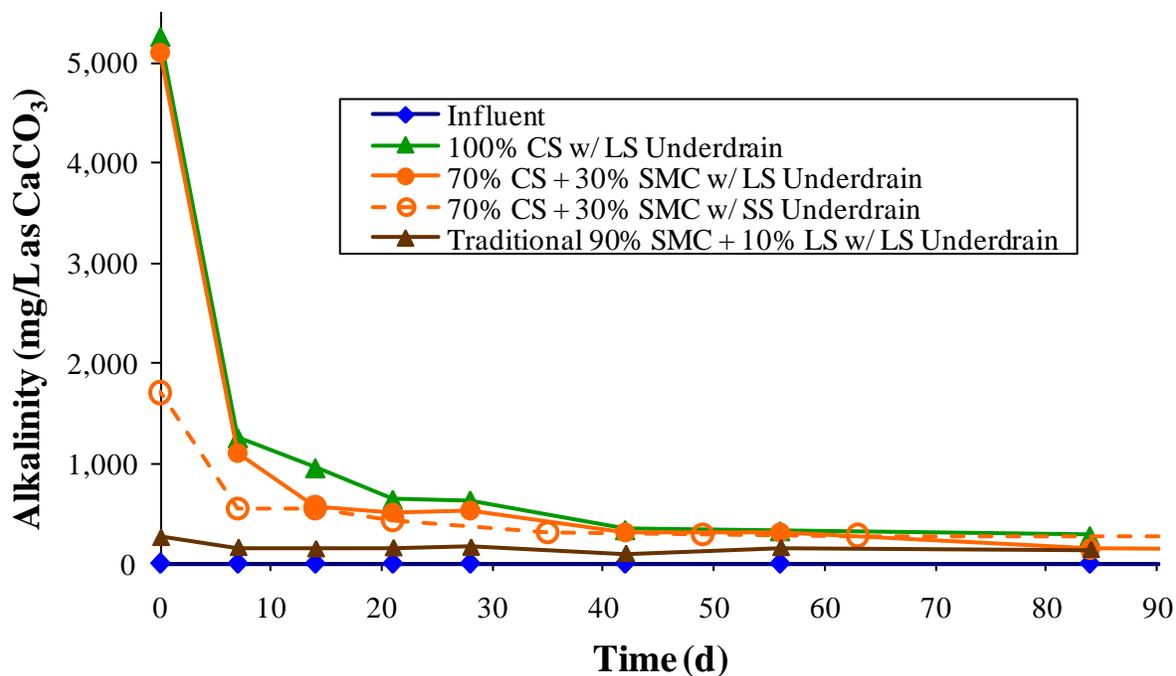


Figure 7. Alkalinity generated from pilot-scale reactors during initial 90 days of the field test.

Metals Removal. Complete removal of dissolved iron (average influent concentration of 71 mg/L) and Al (average influent concentration of 2.9 mg/L) has been maintained thus far *within* all pilot-scale field reactors, and partial manganese removal has also been observed (not shown).

## Discussion

### pH, Alkalinity, Acidity

Previous studies of low-strength MIW (dissolved iron 10-15 mg/L) indicate a strong correlation between the amount of crab shell substrate and alkalinity production (Newcombe and Brennan, 2010). With high-strength MIW from the Klondike-1 site (dissolved iron of 70 mg/L), the laboratory portion of this study was not able to produce similar results. Alkalinity generated in crab shell systems is due to the dissolution of CaCO<sub>3</sub> and also biological activity occurring within the system. Sulfate reduction can produce alkalinity in the form of bicarbonate (HCO<sub>3</sub><sup>-</sup>) according to the reaction shown in Equation 1.



In addition, fermentation byproducts in the form of volatile fatty acids can also produce alkalinity. Previous studies indicate that in crab shell systems treating MIW, half of the alkalinity produced is a result of CaCO<sub>3</sub> dissolution, ¼ is the result of SO<sub>4</sub><sup>2-</sup> reduction, and the remaining ¼ is due to volatile fatty acid production (Robinson-Lora and Brennan, 2009).

The non-linearity of the alkalinity generation in the laboratory column experiment is likely due to compromised microbial activity of the 60% and 80% crab shell columns. These columns experienced clogged lines, which led to a pressure build-up within the column, causing fittings to burst. These events likely allowed the infiltration of oxygen into the column, which impaired the established microbial community. These events occurred early in the experiment, and it appears that neither of these columns ever fully recovered. Thus, alkalinity for these two treatment columns does not fall into line with the expected results as only the dissolution of CaCO<sub>3</sub> was contributing to alkalinity generation.

### Metals Removal

Results show that dissolved Fe was removed initially *within* a majority of the treatment columns. When adequate reducing conditions are met, it is expected that iron will predominate

in its reduced form (ferrous iron,  $\text{Fe}^{2+}$ ). ORP measurements (not shown) indicate reducing conditions near -400mV from the outset of the experiment, so it can be expected that sulfate reduction was occurring. It is possible that sulfate-reduction byproducts (specifically hydrogen sulfide) reacted with the reduced iron species to form iron sulfide ( $\text{FeS}$ ) via the reaction pathways shown in Equations 2 and 3:



If this occurred within the columns, it would be expected that as soon as sulfate reduction ceased, the removal of iron via this mechanism would also come to an end. Unfortunately, sulfate data was inconclusive and could not be used to make any correlations with treatment mechanisms. Previous work (Robinson-Lora and Brennan, 2010) also indicates that sorption to the substrate media itself could account for some of the iron removal occurring within the columns.

Removal of dissolved iron is commonly accomplished in MIW treatment systems via aerobic settling of ferric iron species. In all treatment systems, dissolved iron removal was maintained longer after aerobic settling than within the column itself. Exposure to oxygen after neutralization of the water encourages the oxidation of  $\text{Fe}^{2+}$  to ferric iron ( $\text{Fe}^{3+}$ ) and the subsequent precipitation of  $\text{Fe}^{3+}$  species, primarily (hydr)oxides. This reduction in dissolved iron after the simulated aerobic settling pond was observed in all of the treatment systems. However, complete Fe removal was not achieved in the simulated settling ponds after the 100% crab shell column at the beginning of the experiment. It is postulated that the extremely reducing conditions achieved by the higher fraction of crab shell in this substrate did not allow for Fe oxidation to occur, even after attempted aeration in the simulated settling pond. However, this phenomenon did not occur in the column containing 70% crab shell. The data indicates that mixtures of crab shell and SMC do not experience this phenomenon, making mixed substrates an even more favorable to a pure crab shell substrate when precipitation by aerobic settling is desired.

Removal of dissolved manganese is typically difficult in the remediation of mine influenced waters due to the relatively high pH and alkalinity values required to drive oxidation of  $\text{Mn}^{2+}$  and then subsequent precipitation of  $\text{Mn}^{4+}$  oxides. This work supports previous research (Robinson-

Lora and Brennan, 2009) which has shown that Mn removal can be achieved at significantly lower pH values in systems containing crab shell substrate. It is thought that under the reducing conditions achieved in these systems, precipitation of Mn as rhodochrosite ( $\text{MnCO}_3$ ) is the primary removal mechanism (Robinson-Lora and Brennan, 2011). However, because Mn removal cannot be sustained as long as the removal of other metals, system designs will vary depending on the target metal to be removed.

### **Conclusions**

The data obtained from the continuous-flow column experiment as well as the field data to date from the pilot-scale reactors indicate that a substrate mixture of 70% crab shell and 30% SMC is effective at treating high-strength MIW. The pilot system at the Klondike-1 site will provide valuable scale-up and design information to enable the successful implementation of crab shell systems for future remediation of MIW.

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