RAPID ALKALINITY GENERATION AND METAL REMOVAL FROM MINE IMPACTED WATER USING CRAB-SHELL CHITIN UNDER ABIOTIC CONDITIONS[1]

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Abstract. Crab-shell chitin has proven to be an efficient multifunctional substrate for the biological treatment of mine impacted waters (MIW). Beyond its capacity as an electron donor source, this material has shown high efficiency in the neutralization of acidic water and in the removal of metals, especially Mn. In this study, the performance of crab-shell chitin as a substrate for abiotic and anoxic MIW treatment was assessed to isolate its chemical and physical treatment mechanisms.

Alkalinity generation and metal (Mn, Fe, Al) removal with crab-shell chitin were evaluated and compared to those obtained using limestone in closed-system and kinetic tests. Raw (R-SC20) and deproteinized (DP-SC20) crab-shell chitin were tested and compared to evaluate the effect of chitin-associated proteins. Anoxic, synthetic MIW (SMIW), with individual metal concentrations of 10 mg/L, was used in all tests. Systems for all tests were prepared and operated inside an anaerobic chamber by mixing crab-shell chitin or limestone with SMIW at predetermined ratios.

In closed systems, 5 g/L of R- or DP-SC20 completely removed (≥95%) both Mn and Fe from single-metal SMIW. After 72 h, pH increased from 3 to 9.2-10.2, while 83-187 mg $CaCO_3$/L of alkalinity was generated. In contrast, 5-125 g-limestone/L only raised the pH to 7.8-8.3, leading to lower alkalinity levels (56-63 mg $CaCO_3$/L) and poor metal removal efficiencies (≤85%). In kinetic tests with 5 g-DP-SC20/L, removal of ≥95% of the initial metal load was achieved after 0.5, 6, and 48 h for Al, Fe, and Mn, respectively. Geochemical calculations (PHREEQC) indicate that precipitation of Al-hydroxides and rhodochrosite ($MnCO_3$) and/or $MnHPO_4$ are the probable mechanisms for Al and Mn removal. In the case of iron, geochemical calculations point to hydroxides precipitation; however, visual observations suggest the formation of green rust, a precursor of other more stable phases like goethite or lepidocrocite. The faster changes observed with DP-SC20 compared to limestone could be attributed to its significantly larger surface area. These results are the first to verify and quantify the capacity of crab-shell chitin to treat MIW abiotically.

Additional keywords: Manganese removal, passive treatment

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Introduction

In the search for more efficient ways to passively remediate the very recurrent issue of mine impacted waters (MIW), a great variety of organic substrates have been evaluated. Numerous reports of promising results using waste materials like animal manure, vegetable compost, sawdust, leaf mulch, etc. have been published (Johnson and Hallberg, 2005; Gibert et al., 2002). Crab-shell chitin has also proven to be a promising substrate for the passive treatment of MIW. Rapid pH and alkalinity increases, biological sulfate reduction, and metal removal have been observed under laboratory-batch conditions (Daubert and Brennan, 2007; Korte et al., 2008; Robinson-Lora and Brennan, 2008). Of special interest is the outstanding efficiency of crab-shell chitin to remove Mn compared to other substrates in both laboratory and field studies. In laboratory microcosms tests using spent mushroom compost, sodium lactate, and crab-shell chitin, the latter was the only substrate capable of promoting significant Mn removal in both live and killed systems (>73%, Robinson-Lora and Brennan, 2008). In field studies, enhanced Mn removal (86%) was observed with crab-shell chitin, compared to other substrates (50% for ethanol, wood chips/hay, wood chips/corn stover; Venot et al., 2008).

The rapid changes in pH and alkalinity and a portion of the metal removal have been attributed to the dissolution of chitin-associated carbonates. These carbonates (especially $CaCO_3$ in the form of calcite or aragonite) are naturally present in the shell of crabs and other crustaceans to provide structural strength (Percot et al, 2003). The aim of this study was to evaluate the performance of crab-shell chitin as a substrate for MIW treatment under abiotic and anoxic conditions and to develop a better understanding of the mechanisms that drive the observed changes in systems where metal oxidation is limited. In particular, we focused on the removal of Mn, since this metal has shown to be unusually difficult to remove in most conventional treatment systems.

Materials and Methods

Chemicals

All chemicals used in this study were reagent grade or better. Ultra High Purity argon gas (UHPAG) was provided by MG Industries (Malvern, PA). ChitoRem® SC-20 (minimally processed crab shell), derived from Dungeness crab (JRW Bioremediation, LLC, Lenexa, KS), was used as an example of chitinous material. Raw SC-20 was rinsed with deionized water to remove readily soluble salts and dried overnight at 50°C. The obtained material (R-SC20) was sieved using sieves No. 7 and 140 to remove big particles (>2.80 mm) and fines (< 0.106 mm). Another fraction was deproteinized according to protocols described in previous studies (Percot et al., 2003) using 1 N NaOH; the absorbance of the supernatant was measured at 280 nm, following the completion of the reaction. Particles were then washed with deionized water until neutrality of the rinsate, and dried and sieved as above to produce DP-SC20. Limestone was obtained from a local quarry (Martin Limestone, PA), pulverized using a mortar and pestle, and then sieved using sieves No. 20 and 140 to obtain two particle size fractions: 0.85 – 0.106 mm (particulate) and < 0.106 mm (fine). The chemical composition of all solids (Table 1) was determined by lithium metaborate fusion, followed by ICP-AES analyses (Perkin-Elmer Optima 5300) at the Materials Characterization Laboratory at The Pennsylvania State University. Rock standards were used to calibrate the results. Mineralogical composition of the solids was determined by powder XRD (Scintag, Inc., Cupertino, CA). Calcite was detected as the major component of all three solids, with small quartz impurities in the limestone. The surface area of the solids was measured by physical adsorption of Ar and calculated using the BET (Brunauer, Emmett and Teller) method with a Micrometrics Instrument Corporation ASAP 2010 (Table 1). Sample morphology and composition was observed and measured using a FEI Quanta 200 environmental scanning electron microscope (ESEM) equipped with an Oxford Inca 200 EDS. SEM images reveal the greater porosity of DP-SC20 over limestone, which is coincident with BET results (Fig. 1).

Table 1. Chemical composition and surface area of used solid materials.

Sample	R-SC20	DP-SC20	Limestone
CaO (%)	30.2	35.0	57.0
MgO (%)	1.77	2.5	0.20
SrO (%)	0.32	0.34	<0.05
SiO_2 (%)	<0.05	0.07	0.48
P_2O_5 (%)	3.73	4.99	<0.05
Na_2O (%)	0.49	0.42	<0.05
Al_2O_3 (%)	0.06	0.06	0.41
Fe_2O_3 (%)	0.09	0.04	0.18
MnO (%)	0.04	0.06	<0.01
LOI (%)	63.3	56.5	41.7
Surface area (m^2/g)	14	30	<0.5

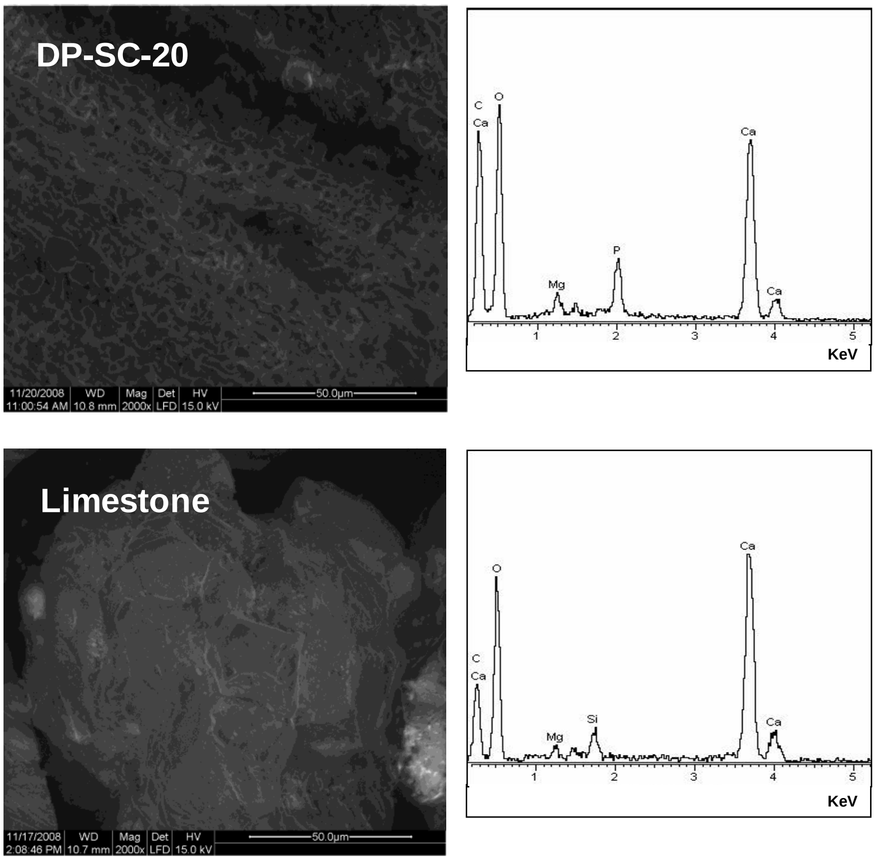

Figure 1. SEM micrographs and EDS spectra of DP-SC20 and limestone.

<u>Synthetic MIW (SMIW) solutions</u>

Tests were conducted using synthetic MIW (SMIW) to limit the affect of other metals (likely present in natural MIW) on the results. SMIW solutions were prepared using Na_2SO_4 (1.4 g/L or 10 mM) as the background salt. Appropriate amounts of $FeCl_2$, $Mn(NO_3)_2$, and/or $Al(NO_3)_3$ were added to generate single or multiple metal (Fe, Mn, and/or Al) solutions at initial concentrations of 10 mg/L for each metal (which are typical metal concentrations found in coal mine drainages in central PA). For additional tests, the Mn concentration was changed to 100 mg/L. The initial pH was adjusted to 3.0 (unless otherwise specified), by adding appropriate amounts of 1 N H_2SO_4. Prior to use, solutions were deaerated with UHPAG for 2 – 3 h and equilibrated in an anaerobic chamber (Coy Laboratory Products, Inc., Grass lakes, MI) for at least 24 h.

Experimental setup

Closed systems. Metal removal capacities of R-SC20, DP-SC20, and limestone were evaluated in closed systems, prepared in glass centrifuge tubes, inside an anaerobic chamber. Filtered (0.2 μm), anoxic SMIW (40 ml) was mixed with predetermined amounts of R-SC20, DP-SC20, or limestone. The final solid load ranged between 2 to 25 g/L for DP-SC20, 2 to 12.5 g/L for R-SC20, and 5 to 125 g/L for limestone. Systems were prepared in triplicate, with duplicate blanks (without solid addition). Tubes were sealed and continuously stirred on an orbital shaker for 72 h. The 72-h contact time was chosen based on preliminary tests conducted in our laboratory to ensure that all chemical transformations in the systems were completed. After the contact time was elapsed, the tubes were opened and the pH of the solution was measured inside the anaerobic chamber. In addition, two subsamples were taken and filtered (0.2 μm). One of the subsamples was promptly (<6 h) analyzed for alkalinity and the other was preserved with 1.5 ml/L conc. HNO_3 for analyses of dissolved metals, S, and P.

Kinetic tests. Kinetic tests were conducted to evaluate Mn removal and alkalinity generation rates using crab-shell chitin under different conditions (Table 2). Reactors (2 L) were operated inside an anaerobic chamber with continuous stirring at 300 rpm. A fixed solid load of 5 g/L (DP- or R-SC20) was used, which was added at t = 0. pH was continuously monitored and duplicate samples (10 ml) were taken at predetermined time intervals of t = 0, 10, 20, and 30 min, and at 1, 2, 6, 12, 24, and 72 h. Samples were filtered (0.2 μm) and promptly (<6 h) analyzed for alkalinity. A subsample was diluted (1:10) and preserved in acidified-anoxic deionized water (2 ml/L conc. HNO_3) for metal, S, and P analyses.

Table 2. Operating conditions for kinetic tests.

System	Fe	Mn	Mn/Fe	Mn/Al	Mn/Fe/Al	Mn100/Fe/Al	Mn pH_o=2	Mn pH_o=4	Mn-aerobic	Mn-RSC20
pH_o	2.92	2.91	2.93	3.12	2.91	3.07	2.00	4.13	3.03	3.02
Mn_o (mg/L)	-	9.6	9.1	10.0	9.9	101.2	9.6	10.1	10.0	10.1
Fe_o (mg/L)	10.1	-	9.1	-	9.6	9.0	-	-	-	-
Al_o (mg/L)	-	-	-	9.2	9.5	9.0	-	-	-	-
Solid	DP-SC20									R-SC20

Analytical methods

Electrodes were used to measure ORP (platinum electrode, ORION 9778 BN), pH (Accumet® BASIC, AB15 connected to a Thermo-ORION pH probe), and NH_4 concentrations

(ISE ORION 9512). Alkalinity was measured by titrations with 0.02 N H_2SO_4 according to the procedure described in Standard Methods (titration end point pH 4.5, APHA, 2005). Dissolved metal, S, and P concentrations were measured by inductively coupled plasma emission spectrometry (ICP, Leeman Labs PS3000UV) at the Materials Characterization Laboratory at The Pennsylvania State University. Volatile fatty acids (VFAs) were determined by high performance liquid chromatography (HPLC, Waters 2695) as described in Robinson-Lora and Brennan (2009).

Statistical analyses of the collected data were performed using MINITAB® statistical software (Minitab Inc., State College, PA). The geochemical computer program PHREEQC (Parkhurst and Appelo, 1999) was used to estimate the saturation indexes (SI) of several Al, Fe, and Mn phases. The concentrations of Cl^- and NO_3^- released from the added metal salts were estimated based on the initial, measured concentration of their associated metals (Fe for Cl^-, and Mn + Al for NO_3^-).

Results

Closed systems

In systems with initial Mn concentrations of 10 mg/L, a solid load of 2 g-DP-SC20/L was able to remove about 89% Mn, while a solid load of 5 g/L achieved >95% removal. Higher Mn removal was observed when higher loads of DP-SC20 were used, achieving 99.7% removal with 25 g-DP-SC20/L (Fig. 2A). Similar results were obtained when R-SC20 was used, with Mn removals of 85 – 97% for solid loads of 2 – 12.5 g/L. In contrast, in systems with a limestone load of 5 g/L, removals of <8% were observed. Even at much higher loads (125 g/L), the addition of limestone (particulate or fine) promoted only 76 and 85% removal of Mn, respectively. In general, higher removals were observed with fine limestone than with the particulate material. Although Mn removal values were significantly different (p-value=0.000) between fine and particulate limestone solids, the differences did not exceed 10%.

After 72 h, the pH of systems amended with DP-SC20 increased from 3 to 9.4 – 10.2 and 67 – 150 mg $CaCO_3$/L of alkalinity was generated (Fig. 2B, 2C). Slightly lower pH values were measured in systems treated with R-SC20 (pH 9.2 – 9.6), yet almost double alkalinity concentrations were reached by the end of the contact time (115 – 223 mg $CaCO_3$/L). In contrast, limestone (particulate or fine) addition only raised the pH to 7.8 – 8.3, and generated much lower alkalinity levels (56 – 63 mg $CaCO_3$/L).

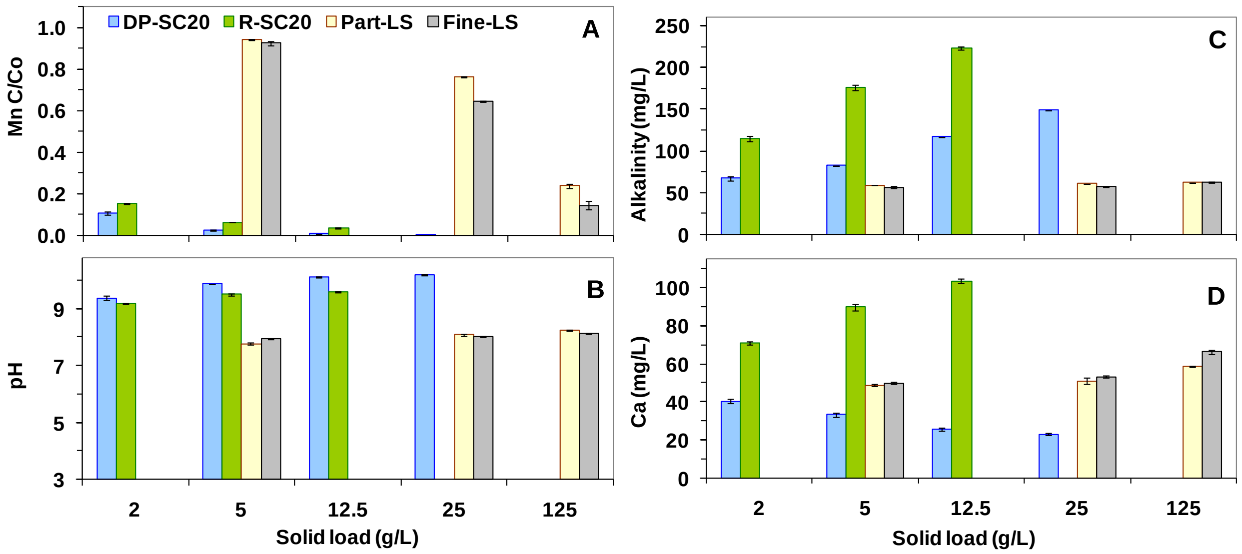

Figure 2. Final manganese concentration (A), pH (B), alkalinity (C), and calcium (D) in systems containing SMIW with initial Mn of 10 mg/L and pH 3.0, treated with DP-SC20, R-SC20, particulate limestone (Part-LS), and fine limestone (Fine-LS). Values represent triplicate averages; error bars represent one standard deviation.

Along with the increase in alkalinity, calcite dissolution from all the evaluated materials resulted in the occurrence of important concentrations of calcium by the end of the test (Fig. 2D). Final Ca concentration increased with the solid load for R-SC20 and limestone and, similar to alkalinity, Ca concentrations were always much higher with R-SC20 (71 – 104 mg/L) than with limestone (49 – 66 mg/L). Systems treated with DP-SC20 exhibited the lowest levels of calcium (23 – 41 mg/L). In addition, an inverse relationship was observed between the final Ca concentration and the solid load in the DP-SC20 systems. The cause of this distinct observation is not clear, but it may be attributed to the occurrence of Ca/Mn co-precipitation.

Kinetic tests

In kinetic tests, rapid changes in pH were observed during the 2 h of the experiment. Systems with single or multiple metals, at initial concentrations of 10 mg/L, reached pH values of 8.9 – 9.9 (Fig. 3A). Similar changes were observed when the reactor was operated under aerobic conditions or when R-SC20 was used (Fig. 3B). The presence of Al and higher Mn concentrations appeared to result in lower pH values, likely due to the formation of Al-hydroxides. Different initial pH values resulted in different rates of pH change (Fig. 3B): the system with pH_o = 4 reached a pH of 9.7 after only 1 h, while the system with pH_o = 2 only reached a final pH of 8.4 by the end of the test.

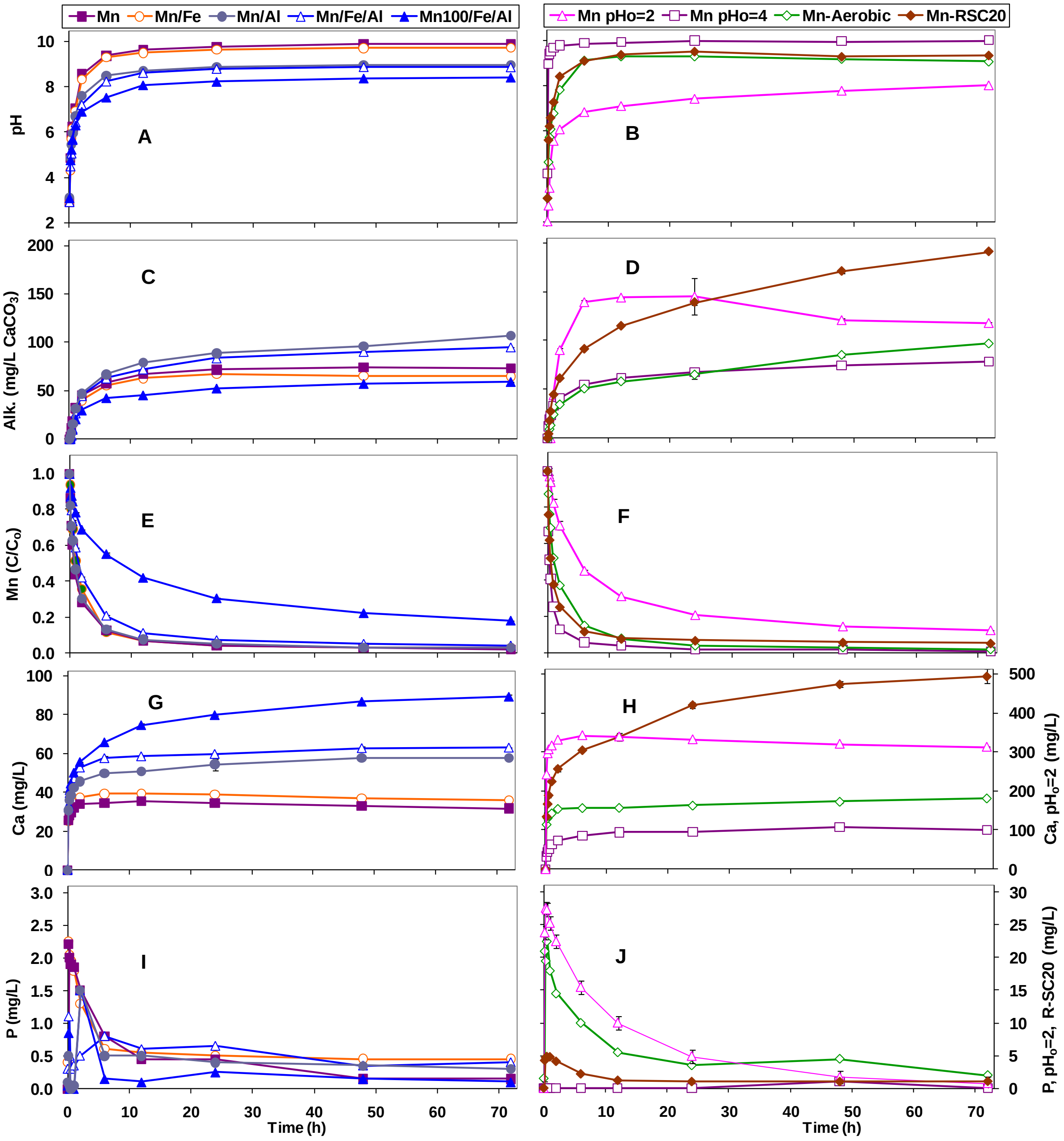

Figure 3. pH, alkalinity, manganese, calcium, and phosphorus changes in reactors containing SMIW and 5 g/L of DP-SC20 or R-SC20 (right panel). Initial metal concentrations were 10 mg/L each, except for Mn100/Fe/Al (left panel), where Mn_o = 100 mg/L. Initial pH was 3.0, and tests were conducted anaerobically, unless otherwise specified (right panel). See detailed experimental conditions in Table 2. Values represent duplicate averages; error bars represent one standard deviation. Note secondary axis for Ca and P for selected data series.

Rapid changes in alkalinity were also observed in all systems (Figs. 3C and D). Changes in most systems were relatively similar, with final concentrations ranging between 64 and 106 mg/L as $CaCO_3$. Lower alkalinity was observed in the system with higher Mn concentrations, while higher alkalinity was generated in the systems with aluminum or lower initial pH. However, in the system with DP-SC20 at $pH_o = 2$, alkalinity levels started to decrease after 24 h, reaching 118 mg/L as $CaCO_3$ by the end of the test. The use of R-SC20 promoted sustained increases in alkalinity and significantly higher (at least two-fold) final alkalinity levels than in the other systems, presumably due to the hydrolysis of chitin-associated proteins.

Removal of ≥95% of the initial Mn load was achieved after 24 h in most systems (Figs. 3E and 3F). Similar results were observed in single- and 2-metal systems, as well as under aerobic conditions, while the presence of the three metals simultaneously or the use of R-SC20 resulted in slightly lower removal (93% at t = 24 h). Even when Mn was increased to 100 mg/L, the addition of 5 g-DP-SC20/L promoted 81.9% removal in 72 h. The initial pH of the SMIW also affected removal: faster removal was achieved with $pH_o = 4$ (>95% after 12 h), while $pH_o = 2$ resulted in a significantly reduced removal (only 87.5% by the end of the test).

The dissolution of the chitin-associated carbonates also resulted in important changes in Ca, (Figs. 3G and 3H). Concentrations rapidly increased during the first 6 h of operation, reaching a plateau. Similar Ca concentrations were reached by the end of the tests for Mn and Mn/Fe systems, as well as under aerobic conditions (32 – 36 mg/L). Lower concentrations were observed when $pH_o = 4$ (20 mg/L). In contrast, higher concentrations were observed in the rest of the systems: when 10 mg/L of Al were present, Ca reached 57 – 63 mg/L, while 100 mg/L of Mn and the use of R-SC20 promoted the release of 89 – 100 mg/L Ca. Tremendously higher Ca concentrations (312 mg/l) were observed when $pH_o = 2$, due to enhanced calcium carbonate dissolution at low pH. In addition, changes in Mg and Sr concentrations were also observed, following very similar trends to those observed with calcium (data not shown). This is not unexpected since Mg and Sr are structurally associated with Ca in the crab shell. However, final Mg and Sr concentrations were much lower than Ca (9 – 40 and 0.6 – 4.8 mg/L, respectively).

Rapid P release was observed in most tests (Figs. 3I and 3J), except when $pH_o = 4$ for which P was below the detection limit (0.05 mg/L) throughout most of the test. The maximum P concentrations were reached within 30 min, without exceeding 2.3 mg/L in most cases. The use of R-SC20 or an initial pH of 2.0 promoted higher P concentrations, reaching 4.75 and

27.6 mg/L, respectively. After this initial peak, P concentrations rapidly decreased, leveling around 0.3 mg/L on average (0.9 mg/L with R-SC20 and $pH_o = 2$) by the end of the test.

In most systems, total (100%) removal of Al and Fe were achieved after 0.5 and 12 h, respectively (Fig. 4). Total removal of Fe was delayed to 48 h when the initial Mn concentration was 100 mg/L. As the pH of the systems increased, Al was released back to the solution after 6 h, resulting in a final Al removal of 58 – 98%. The removal of Fe and Al was also accompanied by the formation of green (in systems with Fe) and white (in systems with Al) precipitates.

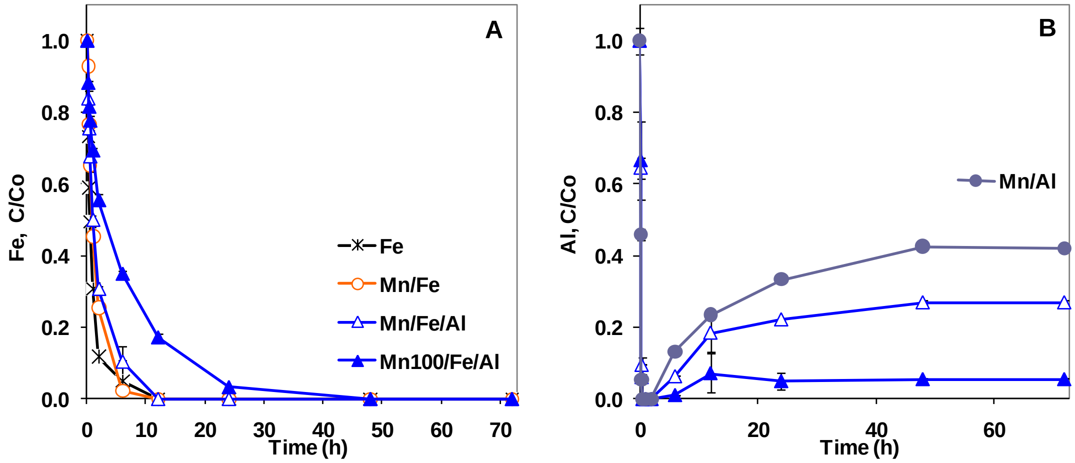

Figure 4. Iron (A) and aluminum (B) changes in reactors containing SMIW and 5 g/L of DP-SC20. Initial metals concentrations were 10 mg/L each, except for Mn100/Fe/Al (panel B), where Mn_o = 100 mg/L, and initial pH was 3.0. Detailed experimental conditions for each test are provided in Table 2.

The almost immediate release of small amounts of formate was observed only when R-SC20 was used. The concentration of formate remained relatively constant during the first 24 h of treatment at around 0.12 mM (4 mg/L). Afterwards, its concentration slowly increased, reaching 0.4 mM (19 mg/L) by the end of the test. Other VFAs (acetate, propionate) were detected only after 48 h of treatment, at concentrations of 0.3 – 0.5 mM (data not shown).

Discussion

Closed systems

Based on the chemical composition of the solids used, limestone particles have about 60% more calcite than crab-shell chitin. However, this higher provision of alkalinity source did not turn into greater pH and alkalinity changes. Under aerated conditions, the presence of atmospheric CO_2 limits the maximum pH achievable with calcite addition to pH ~8.3. However, in this study, tests were conducted in a CO_2-depleted environment for which thermodynamic calculations show that calcite dissolution can result in pH > 9. Several arguments could explain the lower changes observed in systems treated with limestone, compared to those treated with crab-shell chitin. BET analyses and SEM visualization reveal a superior surface area of the R- and DP-SC20 in comparison to that of limestone. Indeed, limestone particles appear much more compact and less porous. According to Stumm and Morgan (1996), the limited surface area of limestone should result in slower dissolution rates, especially once the system has reached near-neutral pH. However, many researchers have argued that BET surface area is not the best parameter to correlate dissolution rates (Cubillas et al., 2005). Authors suggest that not all the measured BET surface area is really available for dissolution and that the use of geometric surface area is a better proxy to report and compare reactive surface areas for $CaCO_3$ dissolution rates. However, when using geometric surface area, normalized dissolution rates of calcite and aragonite were found to be comparable for both abiogenic (pure minerals) and biogenic (bivalves; Cubillas et al., 2005) sources. If this is the case, and since the particle size ranges of the materials used in the present study are similar, the greater BET area and porosity of the crab-shell chitin cannot explain the faster dissolution of its associated carbonates. This suggests that the biogenic character of the chitin-associated carbonates gives them a higher reactivity, making them dissolve more readily. Authors have suggested that the reactivity of different faces of a crystal is different, and that biogenic carbonates may exhibit preferential crystal orientation (Cubillas et al., 2005). This preferential orientation may be responsible for the enhanced dissolution observed here. In addition, the presence of other organic compounds (mainly proteins) associated with chitin in the crab shells represents another major difference between the materials used. After the alkali treatment, a protein residue of < 1% in DP-SC20 is expected (Percot et al., 2003). Under acidic conditions, these proteins can hydrolyze, releasing aminoacids and/or ammonia. The release of these compounds, even at very low concentrations, could have contributed to the higher pH and alkalinity achieved in chitin-treated systems.

While Ca and alkalinity concentrations varied with the load of R- or DP-SC20, final values in limestone-treated systems were very similar, regardless of the loading. In most cases, after 72 h of contact time, less than 2.5% of the initial Ca (based on the solid load) was released from the three types of solids (particulate limestone, fine limestone, and DP-SC20). However, saturation indices (SI) for calcite indicate that all limestone systems were undersaturated, while crab-shell chitin systems were supersaturated with respect to this mineral (Fig. 5). In contrast, the amount of dissolved calcite from R-SC20 was 3 – 5 times higher, resulting in greater final Ca concentrations. In this case, it is suspected that the presence of VFAs, released from the untreated material, promotes higher supersaturation (Stumm and Morgan, 1996).

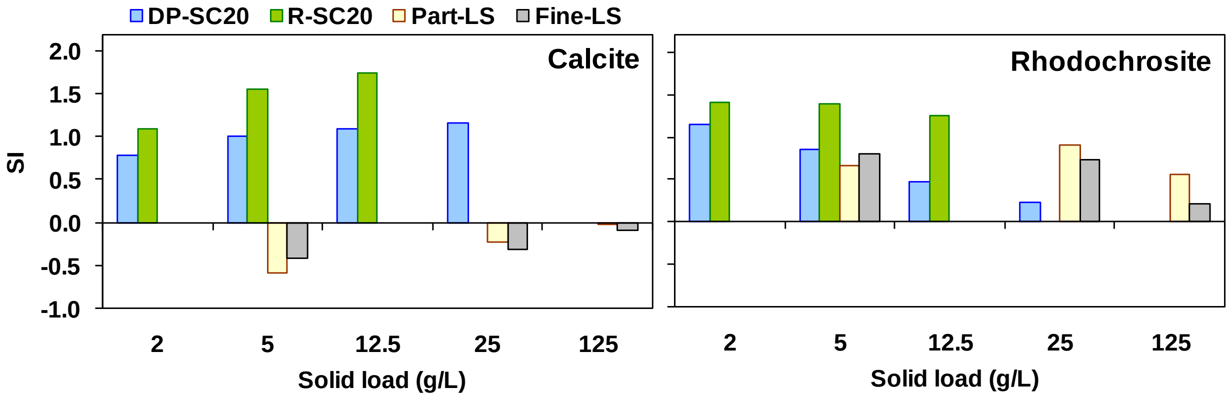

Figure 5. Saturation indices (SI) for calcite ($CaCO_3$) and rhodochrosite ($MnCO_3$) in systems containing SMIW with initial Mn of 10 mg/L and pH 3.0, treated with DP-SC20, R-SC20, particulate, and fine limestone.

In spite of the lower calcium and alkalinity concentrations observed in the limestone systems, geochemical calculations indicate that they, as well as the DP- and R-SC20 systems, are supersaturated with respect to rhodochrosite (Fig. 5). Therefore, it is plausible to suspect that the poor Mn removal observed in the limestone systems is not due to insufficient alkalinity/carbonate provision, but rather to kinetic hindering. Indeed, previous studies have shown that precipitation of manganese carbonates is kinetically regulated (Lebron and Suarez, 1999).

Kinetic tests

The removal of Mn observed in this study can be attributed to sorption and/or (co)precipitation. Sorption onto organic substrates has been already reported to occur in passive MIW treatment (Webb et al, 1998; Willow and Cohen, 2003) and chitin has been identified as promising sorbent for metals like Zn, Cu, Cd, Pb, and Fe (Benguella and Benaissa, 2002; Rae and Gibb, 2003; Karthikeyan, et al., 2005). However, attempts to quantify Mn sorption onto purified chitin in our laboratory have shown no significant interaction between the metal and chitin. On the other hand, Mn can also be sorbed onto the calcite surface, as has been previously reported (Zachara et al., 1991). Co-precipitation of Ca and Mn could also occur: Sibrell et al., (2007) reported significant removal of Mn via this mechanism in pulsed limestone beds, at pH values below 8.3.

From the geochemical point of view, calculated SI values indicate the possible precipitation of several minerals (Fig. 6). In all systems, rhodochrosite supersaturation occurs relatively fast. The formation of manganese carbonates such as rhodochrosite ($MnCO_3$) and kutnahorite ($MnCa(CO_3)_2$) has been previously reported under reductive conditions (Waybrant et al., 1998), as well as in aerated systems (Bamforth et al., 2006). Also, if it is assumed that the measured P released to the system is inorganic P, geochemical calculations point towards the possible precipitation of $MnHPO_4$. This phase is highly insoluble and has been reported to occur when hydroxylapatite is used for the control of acid drainage (Evangelou, 1995). Removal of Mn aided by the presence of phosphates has also been reported in anaerobic digestors via precipitation (Carliell-Marquet and Wheatley, 2002). In addition, the negative charge of the phosphate group can also induce metal sorption. In recent studies, phosphate pretreatment significantly increased the adsorption capacity of rice husk as a sorbent for Pb, Cu, Zn, and Mn removal (Mohan and Sreelakshmi, 2008). However, to corroborate these options, it is necessary to verify the speciation of the released phosphorus with other analytical methods. If phosphate is indeed released, it may represent an additional source of alkalinity. But, given its very low concentrations, its contribution would be significantly lower than that of carbonate.

The most common strategy for Mn removal from aqueous systems is oxidation, which requires high pH since abiotic and biological rates are slow for $pH < 8.0$. Previous researchers have also reported poor Mn removal in the presence of Fe (Johnson and Younger, 2005). In the present study, Mn oxidation can be ruled out since the experiments were performed in an anaerobic chamber, and the removal of Mn and Fe were observed to occur simultaneously. Therefore, the presence of Fe did not negatively influence the removal of Mn. Instead of the typical orange ferric hydroxides, green-colored precipitates were observed in the Fe-containing systems. These precipitates likely correspond to green rust and are an indication that iron oxidation was limited. Calculated SI values indicate the possible formation of iron hydroxides (ferrihydrite, goethite, lepidocrocite), for which (carbonate or sulfate) green rust has been identified as a precursor (Abdelmoula et al., 1996).

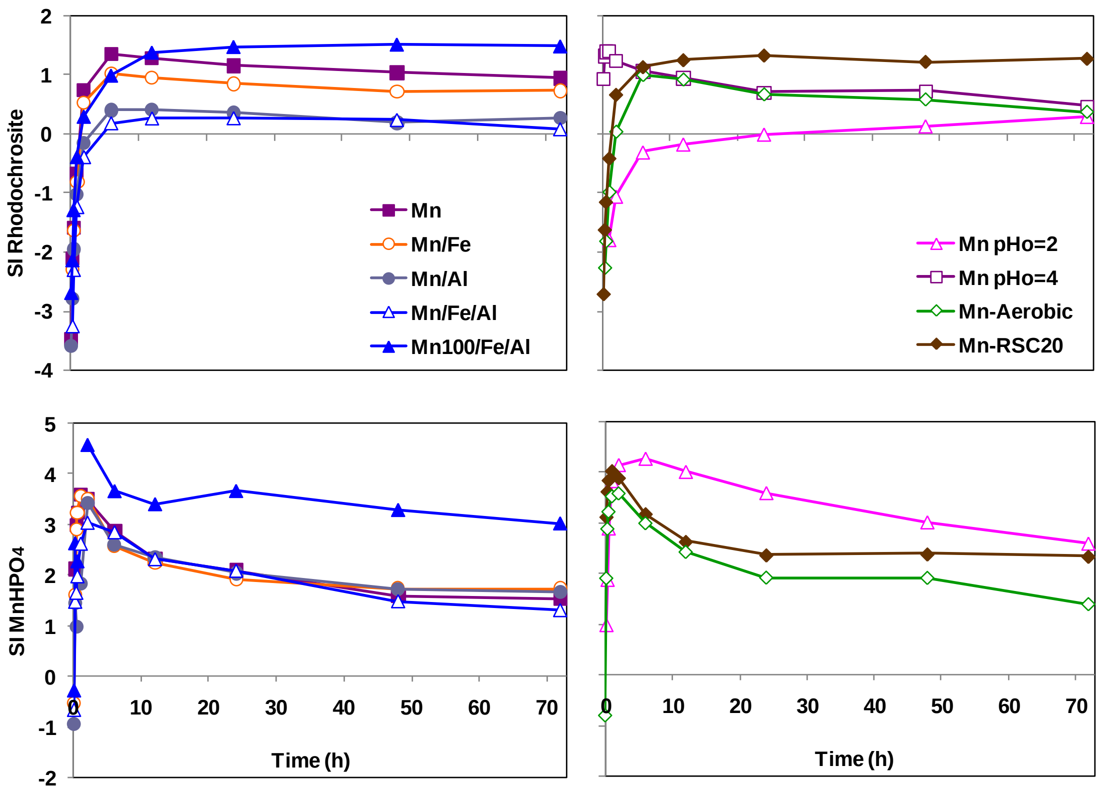

Figure 6. SI values for rhodochrosite ($MnCO_3$) and $MnHPO_4$ in reactors containing SMIW and 5 g/L of DP- or R-SC20. Initial metal concentrations were 10 mg/L each, except for Mn100/Fe/Al (central panel), where Mn_o = 100 mg/L. Initial pH was 3.0, unless otherwise specified (right panel). Detailed experimental conditions for each test are provided in Table 2.

The presence of Al, on the other hand, had some effects on the final pH and alkalinity of the systems, but did not affect Mn removal. In this case, the precipitation of Al hydroxides consumed some hydroxyl ions, leading to lower pH values. Aluminum hydroxides have been shown to act as a sorbent or partner for co-precipitation (Gibert et al., 2005). Therefore, it is likely that Al precipitation partly contributed to the removal of the other metals (Mn and Fe), leading to higher alkalinity values due to the excess carbonate ions that were not used for Mn/Fe precipitation. Aluminum solubility is pH dependant, having a narrow range of pH within which its hydroxides are insoluble (pH 5 – 8). As the pH in the systems continued increasing with time, Al speciation shifted from $Al(OH)_3$ to $Al(OH)_4^-$, leading to partial redissolution. However, it appears that the presence of other metals inhibited the extent of this redissolution, as the lowest amount of Al released back in the system was observed with 100 mg/L of Mn. The redissolution of Al is not desirable but it can be easily limited by controlling the residence time under continuous-flow conditions. Indeed, previous column studies using raw crab-shell chitin, with a 12-h contact time, have reported complete and sustained Al removal (Robinson-Lora and Brennan, 2008).

The similarity between the results obtained for the aerobic test and those obtained under anaerobic conditions indicates the absence of Mn oxidation, in spite of the high pH values reached at early times, and that the Mn removal mechanisms are likely the same as under anaerobic conditions. Furthermore, Mn oxidation is usually characterized by the formation of black precipitates, which were not observed in the present study.

Initial pH of the treated solution had a clear impact on the performance of the systems. The faster changes in pH that occurred when $pH_o = 4$, promoted the fastest Mn removal of all tests. In contrast, the harsher conditions dictated by a lower initial pH ($pH_o = 2.0$) promoted greater dissolution of the chitin-associated carbonates, revealed by the much higher Ca and alkalinity concentrations. These conditions were not enough to promote Mn removal, however. The delay in metal removal may be associated with the lower pH of the system. The decrease in Ca at later times is likely due to calcite re-crystallization and may suggest the occurrence of Mn/Ca co-precipitation.

The much higher calcium concentrations observed in the R-SC20 system indicate that the extent of $CaCO_3$ dissolution was greater than in the systems treated with DP-SC20. This dissolution also led to higher alkalinity levels. The rapid release of formate and other fatty acids is likely due to the hydrolysis of residual proteins present in this minimally processed material, rather than microbial activity. These organic acids could have partially contributed to the higher alkalinity measured with R-SC20. They could also be the cause of the slightly lower Mn removal that was observed, since organic compounds can act as chelating agents, increasing the solubility of metals (Ahumada et al., 2001; Carliell-Marquet and Wheatley, 2002).

Conclusions

Results from the present study demonstrate the potential of crab-shell chitin as a treatment material for abiotic, passive remediation of mine impacted waters. Its greater surface area, combined with an apparently greater reactivity of its chitin-associated carbonates, make it an attractive alternative material for fast alkalinity generation and the treatment of historically difficult Mn-bearing MIW. More research is needed to discern between the possible metal sorption onto chitin or chitin-associated calcite, Ca/Mn co-precipitation, and the role of phosphorus.

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Literature Cited

Abdelmoula, M., Refait, Ph., Drissi, S.H., Mihe, J.P., Genin, J.M.R. 1996. Conversion electron Mossbauer Spectroscopy and X-ray diffraction studies of the formation of carbonate-containing green rust one by corrosion of metallic iron in NaHCO3 and (NaHCO3+NaCl) solutions. Corrosion Science, 38(4): 623–633. http://dx.doi.org/10.1016/0010-938X(95)00153-B.

Ahumada, I., Mendoza, J,. Escudero, P., Ascar L. 2001. Effect of acetate, citrate, and lactate incorporation on distribution of cadmium and copper chemical forms in soil. Communications in Soil Science and Plant Analysis, 32(5): 771-785. http://dx.doi.org/10.1081/CSS-100103908.

American Puclic Health Asociation (APHA) – American Water Works Association (AWWA) – Water Environment Federation (WEF). 2005. Standard Methods for the Examination of Water and Wastewater, 21th ed. Washington, DC.

Bamforth, S.M, Manning, D.A.C., Singleton, I., Younger, P.L., Johnson, K.L. 2006. Manganese removal from mine waters - investigating the occurrence and importance of manganese carbonates. Applied Geochemistry, 21(8): 1274–1287. http://dx.doi.org/10.1016/j.apgeochem.2006.06.004.

Benguella, B., Benaissa, H. 2002. Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies. Water Research, 36: 2463–2474. http://dx.doi.org/10.1016/S0043-1354(01)00459-6.

Carliell-Marquet, C.M., Wheatley, A.D. 2002. Measuring metal and phosphorus speciation in P-rich anaerobic digesters. Water Science and Technology, 45(10): 305–312.

Cubillas, P., Kohler, S., Prieto, M., Chairat, C., Oelkers, E.H. 2005. Experimental determination of the dissolution rates of calcite, aragonite, and bivalves. Chemical Geology, 216:59–77. http://dx.doi.org/10.1016/j.chemgeo.2004.11.009.

Daubert, L. N., Brennan R. A. 2007. Passive remediation of acid mine drainage using crab shell chitin. Environmental Engineering Science, 24 (10): 1353–1358. http://dx.doi.org/10.1089/ees.2006.0199.

Evangelou, V.P. 1995. Pyrite oxidation and its control: solution chemistry, surface chemistry, acid mine drainage (AMD), molecular oxidation mechanisms, microbial role, kinetics, control, ameliorates and limitations, microencapsulation. CRC Press, Boca Raton, FL.

Gibert, O., de Pablo, J., Cortina, J. L., Ayora, C. 2002. Treatment of acid mine drainage by sulfate-reducing bacteria using permeable reactive barriers: A review from laboratory to full-scale experiments. Reviews in Environmental Science and Biotechnology, 1:327–33. http://dx.doi.org/10.1023/A:1023227616422.

Gibert, O., de Pablo, J., Cortina, J. L., Ayora, C. 2005. Municipal compost-based mixture for acid mine drainage bioremediation: Metal retention mechanisms. Applied Geochemistry, 20:1648–1657. http://dx.doi.org/10.1016/j.apgeochem.2005.04.012.

Johnson, D. B., Hallberg K. B. 2005. Acid mine drainage remediation options: a review. Science of the Total Environment, 338: 3–14. http://dx.doi.org/10.1016/j.scitotenv.2004.09.002.

Johnson, K.L., Younger, P.L. 2005. Rapid manganese removal from mine waters using an aerated packed-bed bioreactor. Journal of Environmental Quality, 34(3): 987–993. http://dx.doi.org/10.2134/jeq2004.0300.

Karthikeyan, G., Muthulakshmi Andal, N., Anbalagan, K. 2005. Adsorption studies of iron (III) on chitin. Journal of Chemical Sciences, 117 (6): 663–672. http://dx.doi.org/10.1007/BF02708296.

Korte, K.M., Newcombe, C.E., Brennan, R.A. 2008, Evaluation of three different purities of crab-shell for the remediation of mine impacted water, Proceedings America Society of Mining and Reclamation, 2008 pp 510-524. http://dx.doi.org/10.21000/JASMR08010510.

Lebron, I., Suarez, D.L. 1999. Mechanisms and precipitation rate of rhodochrosite at 25°C as affected by PCO2 and organic ligands. Soil Science Society of America Journal, 63(3): 561–568. http://dx.doi.org/10.2136/sssaj1999.03615995006300030019x.

Mohan, S., Sreelakshmi, G. 2008. Fixed bed column study for heavy metal removal using phosphate treated rice husk. Journal of Hazardous Materials, 153: 75–82. http://dx.doi.org/10.1016/j.jhazmat.2007.08.021.

Parkhurst, D.L., Appelo, C.AJ. 1999. User's guide to PHREEQC (Version 2) – A computer program for speciation, batch-reaction, one-dimension transport and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259.

Percot, A., Viton, C., Domard, A. 2003. Optimization of chitin extraction from shrimp shells. Biomacromolecules, 4:12–18. http://dx.doi.org/10.1021/bm025602k.

Rae IB, Gibb SW. 2003. Removal of metals from aqueous solutions using natural chitinous materials. Water Science and Technology, 47(10):189 – 196.

Robinson-Lora, M.A., Brennan, R.A. 2008, Evaluating crab-shell chitin, lactate, and spent mushroom compost for acid mine drainage remediation in central Pennsylvania, Proceedings America Society of Mining and Reclamation, 2008 pp 911-926 http://dx.doi.org/10.21000/JASMR08010911

Robinson-Lora, M.A., Brennan, R.A. 2009. The use of crab-shell chitin for biological denitrification: Batch and column tests. Bioresource Technology, 100 (2): 534–541. http://dx.doi.org/10.1016/j.biortech.2008.06.052

Sibrell, P. L., Chambers, M. A., Deaguero, A. L., Wildeman, T. R., Reisman, D. J. 2007. An innovative carbonate co-precipitation process for the removal of zinc and manganese from mining impacted waters. Environmental Engineering Science,24: 881–895. http://dx.doi.org/10.1089/ees.2006.012.

Stumm, W., Morgan, J.J. 1996. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. Wiley – Interscience, New York, NY.

Venot, C., Figueroa, L., Brennan, R.A., Wildeman, T.R., Reisman, D., Sieczkowski, M. 2008, Comparing chitin and organic substrates on the National Tunnel Waters in Blackhawk, Colorado for manganese removal, Proceedings America Society of Mining and Reclamation, 2008 pp 1352-1366. http://dx.doi.org/10.21000/JASMR08011352.

Waybrant, K. R., Blowes, D. W., and C. J. Ptacek. 1998. Selection of reactive mixtures for use in permeable reactive walls for treatment of mine drainage. Environmental Science and Technology, 32:1972-1979. http://dx.doi.org/10.1021/es9703335.

Webb, J.S., McGuinnes, S., Lappin-Scott, H.M. 1998. Metal removal by sulfate-reducing bacteria from natural and constructed wetlands. Journal of Applied Microbiology, 84:240–248. http://dx.doi.org/10.1046/j.1365-2672.1998.00337.x

Willow, M. A., Cohen, R. R. H. 2003. pH, dissolved oxygen, and adsorption effects on metal removal in anaerobic bioreactors. Journal of Environmental Quality, 32:1212–1221. http://dx.doi.org/10.2134/jeq2003.1212.

Zachara, J.M., Cowan, C.E., Resch, C.T. 1991. Sorption of divalent metals on calcite. Geochimica et Cosmochimica Acta, 55(6): 1549–1562. http://dx.doi.org/10.1016/0016-7037(91)90127-Q.