

# Passive Treatment of ARD Using Mussel Shells – Part III: Technology Improvement and Future Direction

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## ABSTRACT

Green-lipped mussel is the largest seafood export from New Zealand, producing large amounts of shell waste which ends up in landfills. These shells, and waste mussel meat, provide a novel passive treatment approach for acid rock drainage (ARD). The shells provide a source of alkalinity and the meat provides a carbon source for sulfate-reducing bacteria. Until recently, these systems have been constructed with vertical downward flow. Dissolution of the shells results in precipitation of iron hydroxides on the top of the reactor, while reducing reactions deeper in the system form metal sulfides. The iron hydroxides on the top, however, can eventually reduce permeability.

In this study, three mussel shell reactors were constructed in series to treat ARD. Each reactor was constructed with an up-flow configuration in an attempt to establish reducing conditions throughout the reactor and prevent the formation of iron hydroxides. Inlet chemistry averaged: Fe (108 mg/L), Al (28 mg/L), Zn (6.3 mg/L), Ni (1.4 mg/L), and sulfate (2100 mg/L). The pH was raised from 2.9 to 8 through the reactors and alkalinity was produced. Metal removal rates ranged from 95 % to >99 %. Sulfate concentrations decreased by up to 500 mg/L, dissolved sulfide increased by approximately 60 mg/L, and dissolved oxygen concentrations decreased from near saturation to less than 1 %, all suggesting that reducing conditions were achieved throughout the systems. Microbiology work shows the systems to be dominated by sulfate-reducing bacteria. It is likely that Fe, Zn, and Ni were removed as sulfides. These results suggest that up-flow configurations may be a useful construction technique for mussel shell reactors, especially for ARD with elevated Fe.

Future work includes studies of permeability changes in down-flow reactors as hydroxides accumulate, biogeochemical investigations on both down-flow and up-flow reactors, and the installation of full scale systems using both techniques.

**Keywords:** Mussel Shells, Passive Treatment, Bioreactor

## INTRODUCTION

The green-lipped mussel (*Perna canalicula*) is the largest seafood export from New Zealand. The aquaculture industry produces over 140 000 tons of shells annually (Aquaculture New Zealand, 2010). Native to New Zealand, much of the export is fully shelled mussels, which produces a large amount of shell waste. Although some of the waste is used as a lime amendment by the agricultural industry, much of it ends up in landfills.

Since 2007, various researchers have used waste mussel shells to treat acid mine drainage (AMD) in laboratory experiments, small-scale field trials, and large-scale systems in New Zealand. Mussel shells provide a source of alkalinity, and the associated waste mussel meat and other sea life (about 10 % by mass) provide organic material for sulfate-reducing bacteria (SRB). In the initial early laboratory experiments, the mussel shells were used as a replacement for limestone in typical sulfate-reducing bioreactors containing other sources of organic matter, such as compost, bark chips, and post peel waste strips (McCauley et al., 2009; Mackenzie, 2010; Mackenzie et al., 2011).

Later, large-scale field reactors were constructed with only mussel shells and their associated waste mussel meat. These reactors perform well, removing 96 to 99 % of iron, aluminum, nickel, and zinc and restoring pH from <3 to >7 (Crombie et al., 2011). Autopsy work by Diloreto et al. (in press, 2014) show that the metals are sequestered in distinct zones and in distinct forms within the reactors. The upper layer is dominated by a thick iron hydroxide precipitate, followed by a transition zone, below which is an aluminum hydroxide layer. Zinc sulfides and nickel sulfides are present below the aluminum layer. Mussel shells are nearly completely dissolved away near the surface, becoming more abundant with depth. Redox potential measurements (Eh) show a change with depth, from oxidizing conditions in the upper layers changing to reducing conditions within and below the aluminum hydroxide layer. The pH increases with depth, reaching neutral where shells are most abundant.

Performance of the mussel shell reactors over time is largely unknown. It is likely that the transition zone where conditions change from oxidizing to reducing migrates downward with time as the mussel shells are dissolved. If so, zinc and nickel sulfides precipitated in these layers may be oxidized and the metals released as the oxidation and dissolution front migrates downward. The iron oxide and aluminum layers would likely dominate the system with time, potentially reducing permeability and the system could fail once all the mussel shells have been dissolved.

All the previous systems (laboratory and field trials) were constructed with down-flow configurations. In our current study, we have constructed field-trial mussel shell reactors with an up-flow configuration to determine if reducing conditions would predominate over oxidizing conditions throughout the reactors, and if iron would precipitate as a sulfide rather than as a hydroxide. In addition, increased bicarbonate alkalinity generation in a fully reducing system may slow shell dissolution rates, increasing the lifespan of the systems.

## METHODS

Three passive treatment systems were constructed using 1000 L plastic tubs (standard intermediate bulk containers) with PVC piping, alkathene piping and associated valves, and were installed at an active coal mine to treat AMD. Each system was filled with waste mussel shells from the fishing company Sandford Limited. The mussels were freshly harvested and shelled. The waste shells

contained approximately 10 % waste mussel meat, which included remnants of the green-lipped mussels, whole black-shell mussels, and miscellaneous sea life attached to the shells. Most shells were broken into pieces approximately 5 cm long (Figure 1).



**Figure 1** Mussel shells in completed mussel shell reactor prior to filling with water

The systems were installed in series with an up-flow configuration, such that the inlet was at the base of each system and the water flowed upwards through the shell bed driven by sufficient hydraulic head. Sampling ports were located at the inlet to the three systems, between systems one and two, between systems two and three, and at the outlet from system three. Each system was covered with a tarp to exclude rainfall and sunlight.

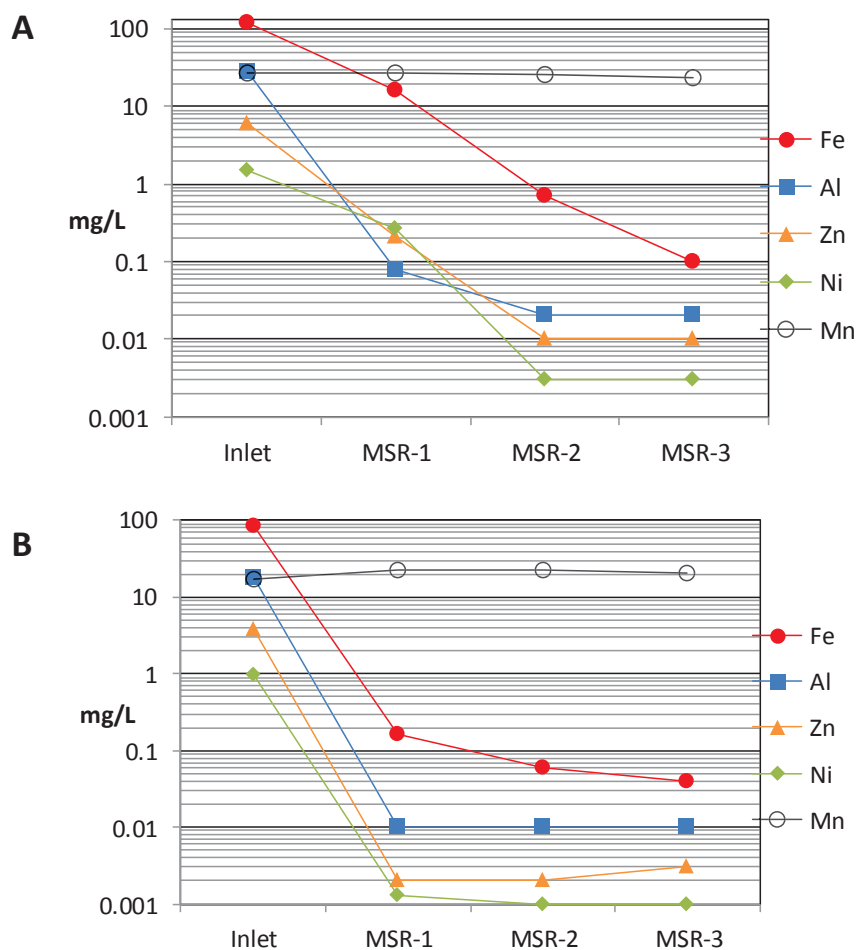
The systems operated for a period of 141 days. Flow rates were varied to determine metal removal for different hydraulic residence times (HRTs). Inlet and outlet samples were collected fortnightly from each system and analyzed for dissolved iron (Fe), aluminum (Al), manganese (Mn), nickel (Ni), zinc (Zn), and calcium (Ca), nitrogen species, dissolved reactive phosphorous, sulfate, and dissolved organic carbon at a New Zealand laboratory using inductively coupled plasma mass spectrometry, colorimetry, ion chromatography, catalytic oxidation, and cadmium reduction techniques. Field measurement included pH, dissolved oxygen, and sulfide. Solid and liquid samples were collected from the top 10 cm of each system for microbiological analysis using Next-Generation Sequencing technologies.

## RESULTS

Flow rates ranged from 40 to 660 ml/min through the system train, equating to HRTs ranging from 14 hours to 232 hours in each of the first two systems. The third system had slightly fewer mussel shells, resulting in a 9 % lower residence time compared to that in each of the first two systems.

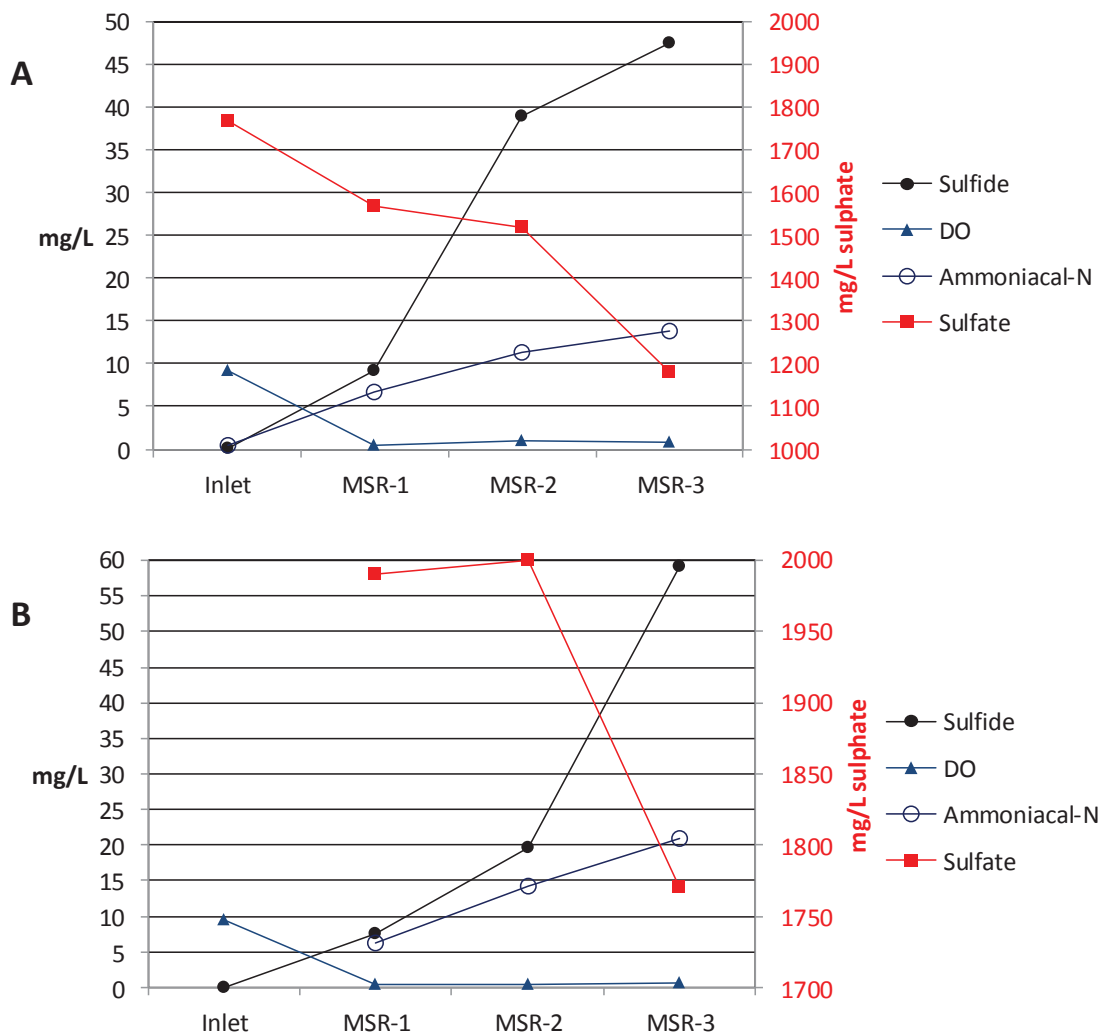
The inlet AMD chemistry is dominated by sulfate (2100 mg/L), Fe (108 mg/L), Al (28 mg/L), and Mn (24 mg/L), with low concentrations of Zn (6.3 mg/L) and Ni (1.4 mg/L). The pH ranges from 2.9 to 3.1. Typically, Fe(II) comprises 5 % of the total Fe, dissolved oxygen is near saturation, and no dissolved sulfide is present.

As the water passes through the systems, the following metal removal rates are achieved: Fe (96 to >99 %), Al (>99 %), Ni (95 to >99 %), Zn (98 to >99 %), and Mn (0 to 22 %) (Figure 2).

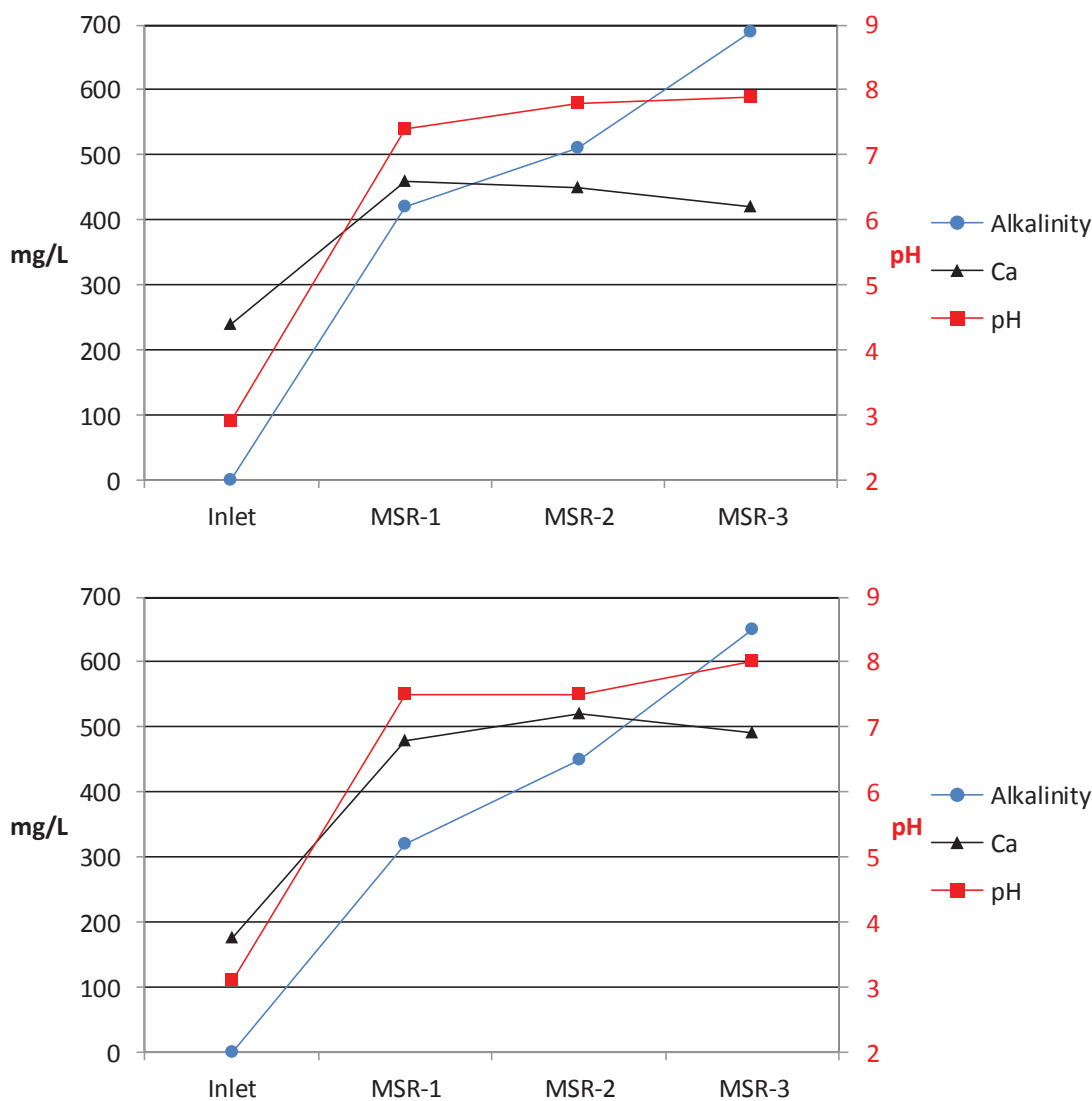


**Figure 2** Concentrations of metals through treatment system. **A** HRT of 28 hours. **B** HRT of 95 hours. MSR-1, mussel shell reactor 1; MSR-2, mussel shell reactor 2; MSR-3, mussel shell reactor 3

Several parameters suggest that reducing conditions are being achieved in the systems. Sulfate concentrations decrease through the systems (by up to 500 mg/L) while dissolved sulfide concentrations increase (by approximately 60 mg/L) (Figure 3). Dissolved oxygen concentrations decrease from near saturation to below 1 % in the first reactor and ammoniacal nitrogen (reduced nitrogen) concentrations increase linearly through the three systems. The pH increases from 3 to 7.5 in the first reactor and shows some increase to near 8 through the second and third reactors (Figure 4). Concentrations of calcium (Ca) increase predominantly in the first reactor, while alkalinity follows a linear trend through the three systems.



**Figure 3** Sulfur species, DO, and ammoniacal nitrogen through treatment system. **A** HRT of 56 hours. **B** HRT of 95 hours. MSR-1, mussel shell reactor 1; MSR-2, mussel shell reactor 2; MSR-3, mussel shell reactor 3



**Figure 4** Alkalinity, calcium, and pH through treatment system. **A** HRT of 56 hours. **B** HRT of 95 hours. MSR-1, mussel shell reactor 1; MSR-2, mussel shell reactor 2; MSR-3, mussel shell reactor 3

Preliminary genomic DNA and RNA-Seq molecular analysis of the substrate shows a succession of bacterial communities through the three reactors. In the first reactor, the microbial community is comprised of bacteria (90 %) and archaea (10 %). The bacteria community is dominated by SRB (such as *Desulfotomaculum* and *Desulfovibrio*) but also contains many methanotrophs (methane-oxidizing bacteria). The second reactor contained some SRB but no methanotrophs. Compared to the first reactor, the SRB only comprised a minor proportion of the entire community. The third reactor did not contain any SRB or methanotrophs, but rather had very generic species such as bacterial halophiles of marine origin, and Firmicutes, such as soil bacteria of the Clostridia class (obligate anaerobes).

After the systems had operated for several months, precipitates were noted on the surface of the water in all three reactors (Figure 5). In the first two, this precipitate exhibited a vein-like and

crystalline-like texture with various colors of grey and tan. In the third reactor it was dominated by yellowish-white crystalline and amorphous material.



Figure 5 Precipitates on the water surface of mussel shell reactors

## DISCUSSION

Neutralization of the AMD and generation of bicarbonate alkalinity is likely occurring through both dissolution of the mussel shells and sulfate reduction by SRB. Almost all of the metal removal by the systems and pH increase is accomplished in the first reactor, with the exception of Mn which shows removal (albeit minimal) in the second and third systems. Changes in dissolved oxygen, ammoniacal nitrogen, and sulfate show that reducing conditions are established in the first reactor, and are enhanced in the second and third reactors, suggesting that the transition metals Fe, Ni, and Zn are likely being removed as sulfides. The presence of SRB in the first two reactors confirms that sulfate reduction is occurring. The presence of methanotrophs in the first reactor show that methane is being produced, which only occurs under strong reducing conditions with an Eh below -150 mV (Wang et. al., 1993).

Aluminum, however, does not form a sulfide in these systems, but rather precipitates as a hydroxide. Manganese also does not form a sulfide in these systems, but rather can precipitate as oxides, hydroxides (Stumm & Morgan, 1996), and carbonates (Bamforth et al., 2006) and can be removed through adsorption onto iron hydroxides. It is unlikely that manganese oxides are forming under these reducing conditions and unlikely that Mn is being adsorbed onto iron hydroxides if most of the Fe is being removed as sulfide. It is possible that the minimal removal of Mn through these systems is occurring through the formation of manganese carbonates, similar to rhodochrosite ( $MnCO_3$ ) or kutnahorite ( $CaMn(CO_3)_2$ ). The formation of these minerals typically requires a pH of greater than eight, which is approached in the third system.

In the second and third reactors, additional alkalinity is produced, the pH is raised slightly higher, and sulfate concentrations are lowered significantly while dissolved sulfide concentrations increase. Minimal dissolution of mussel shells occurs in the second and third reactors, as evidenced by relatively stable, and even decreasing, Ca concentrations. Therefore, the increase in bicarbonate alkalinity in the second and third systems may be due in part to sulfate reduction by SRB. The presence of SRB in the second reactor confirms that sulfate reduction is occurring in that cell,

however, no SRB were detected in the third reactor. The microbiological samples were collected near the top of the reactors. It is possible that SRB may be present in the third reactor at depth.

The precipitates forming on the surfaces of the reactors may be elemental sulfur, since more sulfate is removed from these systems than can be accounted for by dissolved sulfide and the formation of metal sulfides. It is also possible that gypsum is forming on the surfaces, which could explain the decrease in both Ca and sulfate in the third reactor.

The construction of these three systems in series creates a true plug flow reactor (Schmidt & Lanny, 1998). Although short-circuiting is possible within each individual component, short-circuiting through the entire system train is prevented by having three distinct parts to the system. Since sampling can be conducted between each component of the system, the performance and removal mechanisms in each component can be analyzed separately and extrapolated to the potential performance of a full scale system. Construction of trial passive treatment systems in series can provide useful information on treatment performance and metal removal mechanisms.

The up-flow configuration likely contributes to the successful establishment of reducing conditions and likely will lead to minimal formation of iron hydroxides. It is preferable to avoid the formation of iron hydroxides, as this would lead to a decrease in permeability with time, as was noted in a large-scale mussel shell reactor constructed at Stockton Mine, West Coast, New Zealand (Crombie et al., 2011).

Additional up-flow mussel shell reactors have been constructed at the Bellvue abandoned coal mine AMD site on the West Coast of New Zealand (West et al., 2013). Along with mussel shell reactors, a bioreactor containing compost, bark chips, post peel strips, and mussel shells is operating at the Bellvue site to compare the performance of mussel shells with and without an organic matrix. The results from Bellvue and from this study will be used to optimize mussel shell reactor design for other sites in New Zealand.

Future work on mussel shell reactors includes permeability studies, biogeochemical investigations, and installation of full-scale systems. The permeability studies currently underway aim to measure the change in permeability in down-flow reactors as hydroxides accumulate. Biogeochemical investigations are currently underway for both up-flow and down-flow reactors, and several full-scale systems are planned to be installed at AMD sites using both techniques.

## CONCLUSIONS

1. Three small-scale mussel shell reactors were constructed in series at an active coal mine to treat AMD. Unlike previous mussel shell reactors, these were constructed in an up-flow configuration.
2. Inlet water chemistry to the system train had a pH of 2.9 to 3.1, and metal concentrations as follows: Fe (108 mg/L), Al (28 mg/L), Mn (24 mg/L), Zn (6.3 mg/L), and Ni (1.4 mg/L). Sulfate concentrations were 2100 mg/L.
3. Residence times in each of the three reactors ranged from 14 to 232 hours, over an operating period of 141 days.
4. The pH increased to 7 through the first reactor and near 8 through the second and third reactors and the effluent water had net alkalinity.
5. Metal removal rates were as follows: Fe (96 to >99 %), Al (>99 %), Ni (95 to >99 %), Zn (98 to >99 %), and Mn (0 to 22 %). With the exception of Mn, these metals were mostly removed in the first reactor.



6. Sulfate concentrations were lowered by up to 500 mg/L, dissolved sulfide increased by approximately 60 mg/L, DO concentrations decreased from near saturation to less than 1 %, and ammoniacal nitrogen increased through the systems, all suggesting that reducing conditions were achieved in the systems by means of SRB.
7. Sulfate-reducing bacteria were present in the first two reactors, confirming that sulfate reduction is occurring.
8. It is likely that Fe, Zn, and Ni were removed in the system as sulfides, Al as hydroxides, and Mn as carbonates.
9. A crystalline and amorphous precipitate forming on the surface of the reactors may be elemental sulfur with or without gypsum.
10. An up-flow configuration through mussel shell reactors may help to establish and maintain reducing conditions and remove Fe as sulfides rather than hydroxides, thereby maintaining permeability and extending the longevity of these systems.

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