A MODULAR FIELD-BIOREACTOR FOR ACID ROCK DRAINAGE TREATMENT[1]

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Abstract. The paper focuses on the improvements to engineered features of a passive technology that has been used for remediation of acid rock drainage (ARD). This passive remedial technology, a sulfate-reducing bacteria (SRB) bioreactor, takes advantage of the ability of SRB that, if supplied with a source of organic carbon, can increase pH and alkalinity of the water and immobilize metals by precipitating them as metal sulfides or hydroxides.

The remoteness of ARD sites and their abundance require that the design of an SRB bioreactor be simple and inexpensive. Therefore, bioreactors need to be designed to a size that allows for transportation using primitive roads. To satisfy these requirements a design for a modular treatment system was developed using reactive cartridges (RC) that are prefabricated as 2.44-meter diameter vessels. The RC has been designed so it supports the prime functional aspects of a bioreactor such as high permeability, ample supply of organic carbon, ability to maintain anaerobic conditions, and capacity to accumulate precipitated metals and means for their periodical removal, as needed. In addition, the configuration of the RC allows for an easy replacement of the organic carbon. The RCs can be transported to an ARD site and assembled into a treatment system with a number of modules as required by the ARD flow rate and the metals load. A bioreactor system consisting of four RCs will be installed at an abandoned mine site with ARD of pH 5 or lower and a significant load of metals. The process of site selection is in progress.

The RC design was developed by the Mine Waste Technology Program (MWTP) at MSE Technology Applications (MSE), Butte, Montana, USA. The work was funded by the U.S. Environmental Protection Agency (EPA) and was jointly administered by the EPA and the U.S. Department of Energy (DOE) National Energy Technology Laboratory and performed at the Western Environmental Technology Office under DOE contract number DE-AC09-96EW96405.

Additional Key Words: cartridge, walnut shells, corn stover

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[1] Paper presented at the 7th International Conference on Acid Rock Drainage (ICARD), March 26-30, 2006, St. Louis MO. R.I. Barnhisel (ed.) Published by the American Society of Mining and Reclamation (ASMR), 3134 Montavesta Road, Lexington, KY 40502

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7th International Conference on Acid Rock Drainage, 2006 pp 2575-2584

DOI: 10.21000/JASMR06022575

https://doi.org/10.21000/JASMR06022575

Introduction

Acid rock drainage is a typical result of mining sulfide-rich ore bodies. It is formed when sulfide-bearing minerals, particularly pyrite [iron disulfide (FeS_2)], are exposed to oxygen and water as described by the following overall reaction (Equation 1).

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \dashrightarrow Fe(OH)_3 + 2SO_4^{-2} + 4H^+ \qquad (1)$$

This reaction results in increased acidity of the water (lowered pH), increased metal mobility, and the formation of SO_4^{-2}. Acid rock drainage emanates from abandoned and active mines, causing significant environmental problems by contaminating surface waters and groundwater with dissolved metals and raising their acidity.

Because conventional treatment of ARD is often not feasible due to the remoteness of the site, lack of power, and limited site accessibility, passive remedial technology may be appropriate. One such technology uses SRB that have the ability to increase pH and alkalinity of the water and immobilize dissolved metals by precipitating them as metal sulfides, provided that a favorable biochemical environment is created.

When provided with an organic carbon source, SRB are capable of reducing the SO_4^{-2} to soluble sulfide by using sulfate as a terminal electron acceptor. Acetate and $HCO3^-$ ions are also produced. The soluble sulfide reacts with the metals in ARD to form insoluble metal sulfides (Equations 2 and 3). The $HCO3^-$ ions increase pH and alkalinity of the water.

$$SO_4^{-2} + 2CH_2O \dashrightarrow H_2S + 2HCO_3^- \qquad (2)$$

$$H_2S + M^{+2} \dashrightarrow MS + 2H^+, \quad \text{where M = metal} \qquad (3)$$

Such biochemical processes can be advanced in an engineered field bioreactor. Organic carbon, the organic electron donor, represented in Equation 2 by the formula $2CH_2O$, may be provided either by feeding a bioreactor with a chemical compound like lactate or methanol that delivers C directly or can be obtained from a selected organic matter that, if not used for this purpose, may be classified as waste. Because of the remoteness of many abandoned mine sites, the latter option is more appealing as it does not pose the risk of the misuse of methanol by irresponsible parties. Such field bioreactors, successfully operated as reported by Canty (1999), Gusek et al. (2000), and Zaluski et al. (2003), were designed for site-specific conditions and were constructed at individual ARD site using conventional building materials.

The remoteness of ARD sites, their abundance, and economic aspects require that the design of a bioreactor be simple and inexpensive and that the bioreactor be capable of treating the anticipated ARD flow rate and associated dissolved metals loading. Therefore, it is preferred that bioreactors are prefabricated and designed to a size allowing for transportation using primitive and narrow roads in mountainous regions. These conditions are met by bioreactors consisting of a number of modules or reactive cartridges (RC) that are assembled into one SRB treatment system at the mine site.

Construction of a Typical Reactive Cartridge

Organic Matter

Background information. Quite a few organic materials can be used as the organic carbon source (Equation 2) for SRB bioreactors as indicated by MSE (2003) in its Microsoft (MS) Access™ literature database. This database includes the list and references regarding substrate mixture components used in SRB treatment systems and their effectiveness. More than 90 publications that dealt with the use of organic substrates as mixtures for SRB-mediated treatment of ARD were identified. These publications identified 36 organic substrates that included 7 direct and 29 indirect substrates.

The direct substrates are those that do not require decomposition by other microorganisms to provide SRB nutrition. Such substrates include:

- alcohols, e.g., methanol and ethanol;
- organic acids, e.g., acetate, lactate, formate, and pyruvate; and
- sugars, e.g., sucrose.

Indirect substrates are those requiring decomposition by other microorganisms to provide SRB nutrition. These substrates require complex microbial communities to degrade the organic matter and support SRB growth. The publications examined reported quite a variety of such substrates. They can be classified as:

- composts, e.g., spent mushroom compost, leaves;
- wood/paper wastes, e.g., sawdust, leaf mulch, wood chips;
- food production byproducts, e.g., molasses, cheese whey, potato processing waste;
- agricultural products, e.g., hay, straw;
- manure, e.g., cow, horse, dried poultry waste; and
- sewage, e.g., digested sludge, sewage sludge.

The use of direct substrates promises to allow more stringent control of biofouling but requires more complicated reactor design and may not be suitable for remote mine sites. The use of some direct substrates, such as ethanol, at remote mine sites is also complicated by public safety concerns. Indirect substrates are more feasible than direct substrates for low maintenance systems at remote mine sites requiring more long-term operation.

The choice of an effective substrate mixture is dependent on the composition of the ARD and the types of substrates available at low cost. Overall, substrate mixture containing both easily biodegradable materials and slow biodegradable (recalcitrant) materials are the most effective for supporting sustained SRB activity. The easily biodegradable substrate ensures a quick start of a bioreactor. More recalcitrant materials provide the best long-term bioreactor performance.

The substrate mixture should also provide adequate surface area for biofilm development, buffering and adsorption capacity, and adequate hydraulic conductivity. The suitability of a substrate mixture for treating a particular composition of ARD is best determined empirically using laboratory-scale tests. Overall, the literature search indicates that a wide range of organic substrate materials can be used to effectively treat ARD using SRB technology.

Selected Organic Matter. Based on the results of the previous research (Zaluski, 2003, and Figueroa, 2004), a new organic mix consisting of English walnut shells and corn stover was developed by the authors, and was selected as the reactive medium to be used in the RCs at the Silver Cycle Mine. Some advantages of using this mix are listed below.

- Walnut shells are more recalcitrant to biodegradation, thus supporting good long-term operation of a bioreactor.
- Walnut shells provide a solid matrix structure because individual shells actually rest on each other. This structure minimizes time-driven compaction (settling), thus it works toward preservation of the initial permeability of the medium.
- Walnut shells contain a high percentage (56%) of total organic carbon (TOC).
- Corn stover is a widely available crop residual that remains in the field after harvesting of corn cobs. The residual is typically used for animal bedding or fermented for use as animal feed.
- Corn stover contain a high percentage of organic carbon in the form of cellulose that is used by cellulose degrading bacteria to produce substrates easily accepted by SRB.
- Cow manure provides a diverse anaerobic microbial population which includes cellulose degraders and sulfate reducers that ensures a quick startup of the bioreactor. It is widely available and inexpensive.
- Corn stover includes nitrogen needed for healthy microbial activity.

The mix of walnut shells and corn stover is referred to in this paper as W/C organic medium. A ratio value that often follows or precedes this term is the ratio of a bulk volume of one component to the bulk volume of the second component. For example, a 0.6/0.4 W/C mix refers to organic matter consisting of 0.6 bulk volume of walnut shells and 0.4 bulk volume of corn stover measured before they were mixed.

Engineering Features

A modular SRB treatment system consists of a number of RCs that are configured in parallel or in series, depending on the ARD flow rate and its quality (metal load and pH), cleanup objectives, and space available at the given mine site. These RCs are filled with the W/C organic medium of the selected volumetric ratio for each component. The number of the RCs in the treatment system is determined using the BEST (bioreactor economics, size and time of operation) simulator (Zaluski et al., 2005). This simulator has been developed and tailored for designing such a treatment system based on the ARD chemistry and flow rate, and the reactivity of the organic matter that is used as the organic carbon source – the electron donor for the sulfate reduction process.

Flow Configuration. The life span of an SRB bioreactor depends not only on the availability of organic carbon, but also on the permeability of the organic matter. A decrease of the permeability of the bioreactor during its designed operation time may limit the flow rate for the treated ARD and may cause physical encapsulation of organic C, thus making it unavailable for the sulfate reduction process. MSE (2004) investigated time related changes of permeability of organic matter as a function of the flow orientation and composition of the organic matter.

This study included several long-duration permeability tests of an organic matter that included a mix of walnut shells and cow manure (W/M). This organic matter, a predecessor of currently proposed W/C mix, was tested before the latter mix was developed through the combine research of MSE and Colorado School of Mines. The permeability tests were conducted for an upward vertical flow and a horizontal flow to determine the adequacy of each flow configuration for RCs. Results of these tests indicated that the long-term permeability of this medium is significantly higher for flow in a horizontal plane. This phenomenon is attributed to the deformation of the W/M organic medium in which the finest particles are mobilized by the flowing water and migrate downward by gravity to settle at a certain level, usually at the bottom of the container, blocking the flow. In the case of a horizontal configuration, the migrating particles also settle in the bottom of the container; however, they do not block the entry of water that flows above them as it is fed laterally.

The experiments conducted showed that for a horizontal flow configuration the sustainable hydraulic conductivity (K) of the W/M mixture is 0.01 cm/s or higher. In general, K value of the 0.5/0.5 W/M organic medium was one order of magnitude smaller than the K value for the 0.8/0.2 W/M medium. With the use of corn stover that has lower content of fine particles than manure the K value is expected to be higher.

RC Design. Reactive cartridges can be built using commercially available cylindrical or cuboidal high-density polyethylene (HDPE) or polypropylene tanks. Such a tank, used as a vessel to house bags with organic medium, is equipped with necessary features to preserve anaerobic conditions, control the flow and provide for an easy maintenance, thus serving as RC. These modifications are made in a machine shop and then the tank is transported to a mine site. At the mine site the tank can be installed, either aboveground or belowground as required by the site conditions. An appropriate piping system can convey the ARD into the RC. Figure 1 illustrates a cylindrical RC installed belowground at the mine site. Such installation can take advantage of a small pond where ARD accumulates and then can be piped by gravity to the RC.

Any tank of a suitable size and shape can be adapted for the RC; its suitability is determined by the mine site conditions, transportation restrictions, availability, price, etc. The RC design presented in this paper includes a 2.44-meter diameter, 2.44-meter tall polypropylene tank of the nominal size of 9.5 m^3. The 2.44-meter diameter tank was selected for the design because of U.S. Department of Transportation regulations limit the width of the standard load to 8 feet (2.44 m). Figure 2 and Figure 3 are conceptual drawings showing main components of the RC.

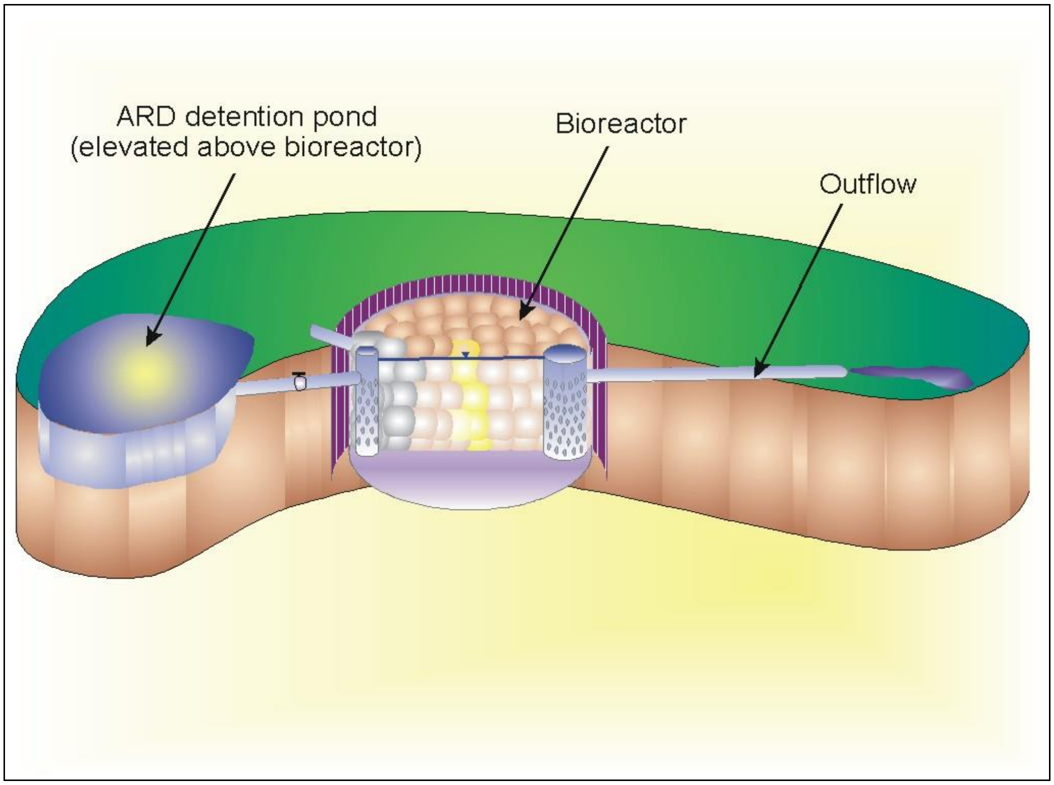

Figure 1. Conceptual picture of the RC installed at the mine site.

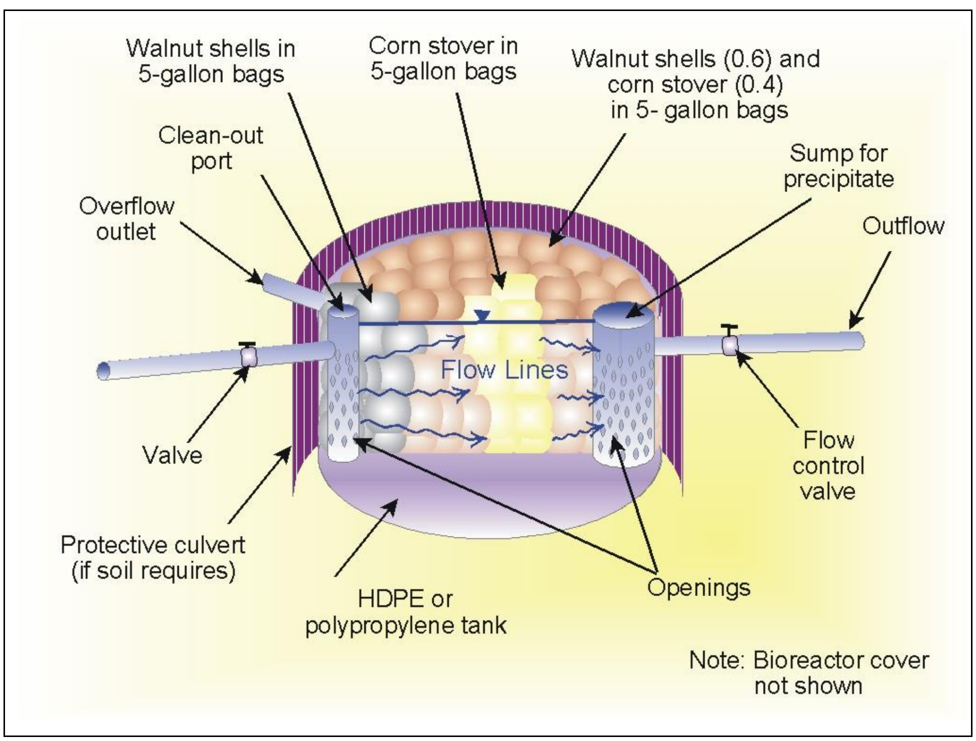

Figure 2. Conceptual 3-dimensional drawing showing main components of the RC.

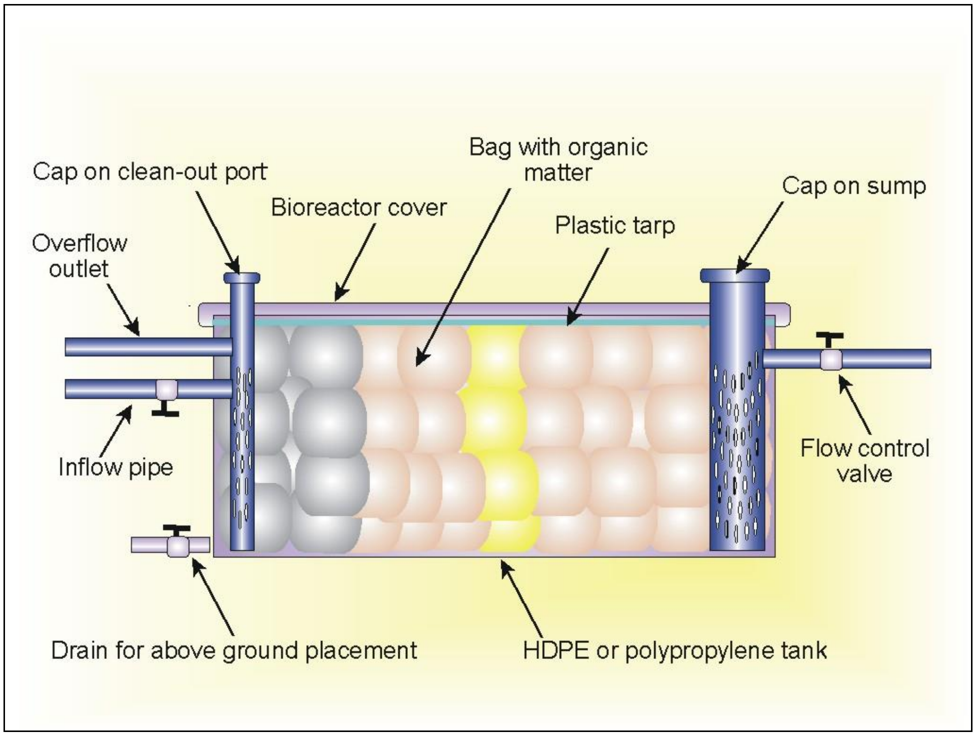

Figure 3. Conceptual cross sectional picture of RC with respective details

Main components of the RC are listed below.

- The round cylindrical tank with its top cut off.
- A 0.1-meter diameter PVC vertical pipe with perforation. This pipe, located at the inlet portion of the RC, serves as a distribution system to "spread" the ARD throughout the entire height of the RC. This pipe is also a cleanout access for agitating and removing $Al(OH)_3$ and $Fe(OH)_3$ that are notorious for precipitating at the inlet of an SRB bioreactor. A jetting tool and/or a suction pump could be used for agitating the precipitate and removing it, respectively.
- A 0.25-meter diameter PVC vertical pipe with perforation. This pipe, located at the outlet of the RC, is a sump for metal sulfides precipitating in the RC. The large diameter of this pipe facilitates easy access to the bottom of the pipe for precipitate removal using a suction pump.
- The inlet pipe to convey the ARD from the mine audit, pond, or from another hydraulically upgradient source to the RC. The inlet pipe may be equipped with a globe valve to control the flow rate.
- The outlet pipe to evacuate treated ARD from the bioreactor. The outlet pipe is located high on the wall of the RC to allow for "deposition" of metal sulfides within the lower portion of the RC. The inlet pipe is equipped with a globe valve to control the flow rate at the downstream side of the RC (preferred).

- The overflow pipe, which is connected to the 0.1-meter diameter pipe, to accommodate excess of ARD.
- The drainpipe, with a valve, is used to drain the RC installed aboveground, if needed.
- Active organic medium bagged in 0.019 m^3 socks of plastic mesh (Figure 4).
- Bags (0.019 m^3) with walnut shells (shown in Figure 3) placed around the distribution pipe. These bags with material of higher hydraulic conductivity reduce the impact of $Al(OH)_3$ and $Fe(OH)_3$ deposition.
- Bags filled only with corn stover, which is less permeable organic matter, are placed in the center of the RC to divert the flow around them.
- A plastic tarp placed on the top of the bags with active organic medium tucked between these bags and the tank walls to create anaerobic conditions in the RC.
- Bags with walnut shells placed above the active organic medium to support the usually dome-shaped cover and prevent it from caving from incidental or vandalistic events.
- A bioreactor cover made from the top of the tank that was previously cut off. The lid is fastened to the tank using appropriate latches.
- Caps for the distribution pipe and the sump to prevent atmospheric oxygen from entering the RC.
- A metal culvert (optional), if the soils around a belowground-placed tank are instable and may cause the tank walls to collapse during replacement of the organic medium (the tank will not collapse when filled with organic medium bags and water).

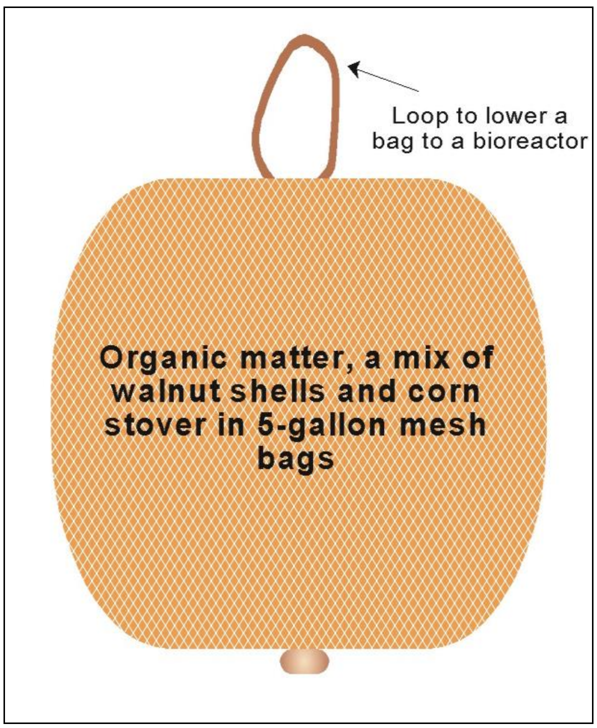

Figure 4. Bag with organic matter (walnut shells and corn stover).

Organic Media Bags. Organic media are bagged in a plastic net, e.g., Peacon Bag Co. braided net, which when laid flat is 0.36-meter wide with 0.1 m openings. This netting material is available in the form of a sleeve. This sleeve is cut to the length of 3 m, folded to the length of 1.5 m to create a double layer sleeve, tied at one end using duct tape to make it a sack, placed in a 0.019 m^3 bucket, filled with appropriate organic medium, and tied at the top in the form of a loop (also using duct tape). The loop is made to facilitate lowering or removing the bag from the RC using a rod with a hook end.

Logistics of Construction and Field Installation. After the tank adaptation work is completed, the RC tank or tanks (depending on the SRB system design) are transported to the mine site using a flatbed pickup. At the site, the tanks are installed above- or belowground depending on the site topography, winter temperature, feasibility of excavation for the tanks, etc. The ARD is piped to the tanks by gravity, preferably from a detention pond that would create a constant (or close to) hydraulic head differential between the ARD source (the pond) and the RC tank. The SRB treatment system usually includes RCs configured in parallel. However, for a small drainage rate but high metals load, the RCs may be configured in series.

Bags with organic medium may be prepared in advance and then transported to the mine site, or they may be made at the mine site. Bags are lowered to an empty RC in layers. After each layer is completed, the ARD is allowed to flow into the RC and saturate the organic medium and enhance tight packing of the bags. Then, the next layer of bags with the organic medium is placed on top of the previous layer, and again more ARD is introduced to the RC.

A total of 494 bags of organic medium and 26 bags of walnut shells are needed to fill up one 9.5 m^3 nominal size RC. Bags with walnut shells are placed in the RC adjacent to the ARD distribution pipe to "envelope" it by the more permeable and porous medium that would facilitate agitating and removal of $Al(OH)_3$ and $Fe(OH)_3$ precipitate. Some walnut shells bags are also placed just under the RC lid (Figure 3) to protect the lid from caving in.

Approximate cost of constructing one RC is $4,000. Installation of an RC at the mine site and filling it with the organic matter add another $4,000, bringing the overall cost for one RC installed at the mine site to the total of $8,000 (2004 U.S. dollars).

Path Forward

A bioreactor system consisting of four RCs will be installed at an abandoned mine site with ARD of pH 5 or lower and a significant load of metals. The site selection process is in progress. Performance of these RCs will be monitored through a MWTP research project implemented by MSE in cooperation with Colorado School of Mines in Golden, Colorado. The primary goal of this project is to demonstrate the successful, long-term performance of SRB RCs. To accomplish this primary goal three specific objectives will be realized by the project. These objectives are: 1) test the long term permeability and performance of the RCs, 2) test the sustainability and functionality of a newly-formulated, organic substrate consisting of walnut shells and corn stover and manure, and 3) track in-situ changes in the composition of the organic substrate and microbial activity with time.

Acknowledgements

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