ADVANCES IN DEVELOPMENT OF BIOREACTORS APPLICABLE TO THE TREATMENT OF ARD[1]

Suzzann Nordwick[2], Marek Zaluski, Brian Park, and Diana Bless

Abstract. Over the past 15 years, MSE Technology Applications has conducted several notable technology demonstrations of biologically based technologies to treat acid rock drainage (ARD). These projects have progressively evolved under the U.S. Environmental Protection Agency's Mine Waste Technology Program (MWTP) and have resulted in significant advances in the development of bioreactor application of sulfate-reducing bacteria (SRB) technology. In this paper, summary information from four separate demonstration projects will be presented for the purpose of providing overviews of the bioreactor design parameters and the operation and development of each bioreactor system. Test methods and data analysis information for each project is not fully provided within this paper, as it is available from other sources. Summarized treatment results will be presented in this paper for three field-demonstrations. Additionally, results of one laboratory design project will be presented. A different bioreactor configuration was employed for each of the four projects. The first design to be presented will be an in situ bioreactor. This configuration was installed within the flooded subsurface workings of the Lilly Orphan Boy Mine in Montana and was operated between 1994 and 2005. The second design to be presented will be a set of on-site SRB bioreactors that were configured in parallel at the Calliope Mine in Montana. These test bioreactors allowed various operational attributes to be evaluated including lime pretreatment and temperature. The configuration of the third design to be presented will be a set of both anaerobic and aerobic bioreactors in staged fashion at the Surething Mine in Montana. This bioreactor design has been in operation since 2001 and shows the comprehensive applicability for biological treatment of ARD. The focus of the last project to be presented will be an investigative approach to bioreactor design. This resulted in a proposed bioreactor configuration to effectively treat ARD by reducing dissolved sulfate and heavy metals concentrations. In general, MWTP results from these four bioreactor configurations show that SRB bioreactors are effective for passive ARD treatment.

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Introduction

Demonstrations conducted under the Mine Waste Technology Program (MWTP) have lead to technical advances in the development of bioreactor application of SO_4^{-2}-reducing bacteria (SRB) technology to treat acid rock drainage (ARD). Benefits of this technology include the reduction of dissolved metal ions to insoluble metal sulfides and the neutralization of the ARD resulting from the production of HCO_3^- from the oxidation of organic nutrients by the SRB. Over the past 15 years, MSE has conducted many bench-scale and design tests along with several pilot-scale field demonstrations. This paper will address engineering design criteria including the selection of organic media, maintenance of system permeability, and strategies for complete mitigation of acid drainage.

Applications and results from four field-demonstrated bioreactor designs will be presented. The first design is an in situ bioreactor in flooded subsurface mine workings. This has been in operation since 1994. The second design is a set of bioreactors that allowed various operational attributes to be evaluated including pretreatment and operational temperature. This demonstration was conducted over a three-year period. The third design focused on the effectiveness of SRB to reduce dissolved sulfate and heavy metals. This system operated from 2001 into 2003. The fourth design is a set of both anaerobic and aerobic bioreactors that operate in staged fashion to show the comprehensiveness of bioreactor applications for ARD treatment.

Background

Acid rock drainage (ARD) results when metal sulfide minerals, particularly Fe pyrite, come in contact with oxygen and water. The metal sulfide minerals are oxidized and then dissolved into the water. ARD emanates from many abandoned mines, which then results in environmental problems by contaminating surface waters and groundwater with dissolved metals, raising their acidity. Conventional treatment of ARD is often not feasible due to the remoteness of the site, the lack of power, and limited site accessibility. To immobilize metals and increase the pH at these sites, passive remedial technologies are needed.

Over the past decade, the MWTP, which is funded by the United States Environmental Protection Agency, has been demonstrating the use of SRB to treat ARD. As shown in Reaction 1, the SRB biological metabolism process uses organic C as an electron donor to reduce SO_4^{-2} to sulfide in the form of H_2S. Bicarbonate ions are also produced. As shown in Reaction 2, H_2S reacts with most dissolved metal ions to precipitate stable metal sulfides. Besides lowering the concentrations of SO_4^{-2} and dissolved metals, the SRB process also produces alkalinity in the form of bicarbonate. This acts to buffer and decrease the acidity of the ARD.

$$SO_4^{-2} + 2CH_2O \rightarrow H_2S + 2\,HCO_3^- \qquad (1)$$

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

Biological SO_4^{-2} reduction, with the subsequent precipitation of metal sulfides, is not the only metal removal mechanism associated with an organic-based system. Other possible treatment processes include ion exchange of metals by an organic-rich substrate, precipitation of metal hydroxides, and the sequential adsorption of metals by precipitated $Fe(OH)_3$. The adsorption of metals by the organic substrate takes place as metal ions are bonded onto organic matter in the substrate. Along with SRB activities, this mechanism plays an initial metal removal role. However, in most cases, the ion exchange of metals only works as a temporary retention of metals, as the mechanisms are pH-dependent and different metals have different adsorption affinities. Over time, more poorly adsorbed metals such as Mn may be released back into solution in exchange for better adsorbed metals. Additionally, adsorption of metals by organic materials is a process limited by and dependent on the amount of organic material present.

Several MWTP SRB-based research demonstration projects involved constructing, operating, and designing bioreactors for ARD treatment. The following four sections contain summaries of individual MWTP projects.

SRB Subsurface Bioreactor

From 1994 to 2005, the MWTP demonstrated an innovative, in situ biological technology to treat and control ARD emanating from the abandoned and remote Lilly/Orphan Boy Mine near Helena, Montana. Cables suspend platforms about 9 meters below the static water level in the mineshaft. Organic matter, a mix of cow manure and straw, was placed on the platforms directly in the shaft, forcing the ARD (upwelling in the shaft) to pass through the organic matter. A cross-sectional view of the underground configuration is shown in Fig. 1. The biological reaction takes place in the substrate regions, and the treated water subsequently flows out of the mine through the portal. Because the technology causes the shaft water pH to rise and the E_H to fall, the amount of acid leaving the mine is decreased. The bioreactor was activated in August 1994 and analytical data taken since has shown a significant and continuous reduction in metals concentrations. Also, the discharge pH has been effectively lowered from a historic level of near 3 to a more neutral pH of near 6.

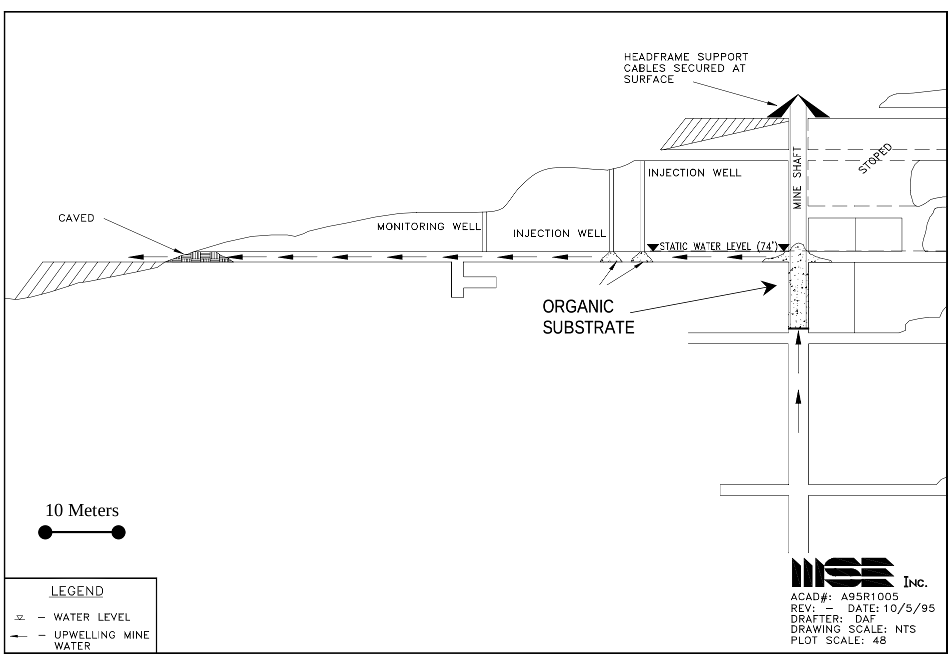


Figure 1. Cross-section of underground mine subsurface SRB bioreactor.

The main purpose of conducting this field demonstration is to evaluate the use of SRB to mitigate metal-contaminated ARD in situ. The performance of the SRB system was monitored through the collection and analysis of samples at multiple locations within the mine tunnel. Principally, dissolved metals concentrations were collected from the mine tunnel using monitoring wells and at the portal. Data collection also included total metals, alkalinity, temperature, dissolved oxygen, pH, E_H, sulfate, sulfide, biochemical oxygen demand, chemical oxygen demand, and volatile fatty acids. Nearly all of the analytical parameters showed positive trends toward the treatment of ARD. However, more desirable results were observed in the tunnel than at the portal. An in-depth discussion of the project has been the subject of previous publications (Canty, 1999; Canty, 2000; and Nordwick et al., 2003).

The chemical parameters typical to untreated Lilly/Orphan Boy Mine water as are shown in Table 1 along with laboratory-obtained typical dissolved metals and post treatment water chemistries for the tunnel water and mine portal effluent.

Table 1. Typical Lilly/Orphan Boy ARD and SRB treated water chemistries.

	Iron (mg/L)	Zinc (mg/L)	Aluminum (mg/L)	Manganese (mg/L)	Arsenic (mg/L)	Cadmium (mg/L)	Copper (mg/L)	Sulfate (mg/L)	pH
ARD	27.7	26.1	9.69	6.21	1.07	0.33	0.32	277	3.0
Tunnel	9.7	<0.01	<0.02	1.51	0.04	<0.005	<0.002	21.0	6.6
Portal	28.4	12.5	0.51	5.44	3.66	0.064	0.041	223	5.2

The data shows that the portal effluent removal efficiencies are greatly affected by spring runoff and that the overall metal removal is extremely high for Al, Cd, Cu, and Zn, but lower for As and Fe. The data also indicates that higher metal removals were obtained within the tunnel than at the portal. This phenomenon is attributed to the treated water being recontaminated with historic metal precipitates in the tunnel and by additional ARD infiltration from fractures within the tunnel as it travels through the section of tunnel beyond the organic substrate to the portal.

The pH of the mine water increased almost immediately after the implementation of the technology. This initial increase in pH was attributed to the buffering capacity of the organic substrate. During spring runoffs, the pH and water quality are lower in the portal than in the tunnel where the pH stays near neutral. This could be due to oxygenated surface water runoff penetrating through the ground above the portal, flowing into the tunnel, and then solubilizing historic metal precipitates and becoming contaminated as it passed through the tunnel. Also, the spring water quality may decrease at the portal due to a greater amount of ARD infiltration from fractures within the tunnel walls and a greater amount of recontamination resulting from water flow over the historic metal precipitates within the tunnel.

On-Site SRB Bioreactor

The primary objective of this project was to assess various configurations of bioreactors and monitor their ability to produce a high-quality effluent. This project was preformed to demonstrate that passive SRB technology could be used for remediation of thousands of abandoned mine sites that emanate ARD. A total of three SRB bioreactors were configured for horizontal flow and designed to evaluate the SRB technology applied in different conditions, and were constructed at the Calliope Mine site in the vicinity of Butte, Montana. Two underground bioreactors were built. One of these had a limestone cobble pretreatment section that was added to evaluate its efficiency effect on SRB to induce an improved pH and oxidation-reduction potential. However, conclusions on the pretreatment section could not be made as weather changes caused a significant improvement of the ARD quality. The third bioreactor had a pretreatment section and was built aboveground to evaluate the effect of cold weather and freezing on the system. Results did demonstrate that winter freezing of a well-established SRB population has little or no effect on SRB activity during the rest of the year.

Each bioreactor was filled with a combination of organic matter, limestone, and cobbles placed in two or four chambers. A simplified bioreactor cross-section is shown in Fig. 2.

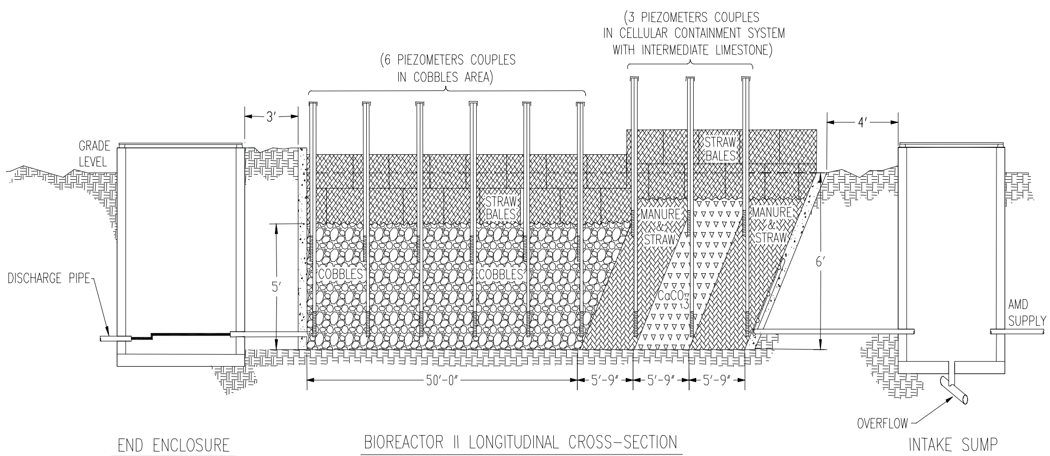


Figure 2. Cross-section of SRB bioreactor to treat ARD.

The belowground bioreactor with the pretreatment section was 21.8 m (71.5 ft) in length and the other was 18.6 m (61 ft). Both were constructed in 4.3-m (14-ft) top-wide with 1.2-m (4-ft) bottom-wide trapezoidal trenches. The aboveground bioreactor was 22.1 m (72.5 ft) in length and constructed in a 3.7-m (12-ft) wide metal half-culvert. The chambers were filled with organic matter or limestone and each were 1.5 m (5 ft) in length. The operation flow rate was 3.785 liters (1 gallon) per minute and corresponded to a calculated 5-½ day residence time for the ARD in the bioreactors with the pretreatment section and a 4-½ day residence time for the other bioreactor.

The organic matter was provided as an 80% to 20% by volume mixture of cow manure and cut straw. The cut straw was added to provide secondary porosity to the mix. TerraCell™ material, commonly used in landscaping for slope stabilization and made of high-density polyethylene, was used to form a cellular containment system (CCS) to house the organic matter (Zaluski et al., 2001, and Zaluski and Manchester, 2001). The CCS prevented the organic matter from settling to the bottom of the bioreactor, thus fostering the flow of ARD through the entire cross-sectional area without channeling. Each layer (lift) of TerraCell™ was positioned at 60 degrees off the horizontal plane so that the cells of each lift would be partially offset with respect to the cells of adjacent lifts. Each lift was 15.2 cm (6 in) thick and contained 27.9-cm (11-in) by 21.6-cm (8.5-in rhombohedral-shaped cells.

The bioreactors operated from December 1998 to July 2001 and previous publications have included a more in-depth discussion of the project details (Zaluski et al., 1999; Zaluski et al., 2000; Zaluski et al., 2001; and Zaluski et al., 2003). Bioreactor performance was monitored monthly by recording dissolved metals, pH, E_H, dissolved oxygen, and temperature measurements of both the influent and effluents. Analysis included SRB population, alkalinity, sulfate, sulfide, and dissolved metals concentrations. The chemical parameters typical to untreated Calliope water are shown in Table 2 along with the typical dissolved metals and post treatment water chemistry.

Table 2. Typical Calliope Mine site and bioreactor effluent water chemistries.

	Iron (mg/L)	Aluminum (mg/L)	Manganese (mg/L)	Arsenic (mg/L)	Cadmium (mg/L)	Copper (mg/L)	pH
Feed	2.96	8.8	2.86	0.003	0.031	2.09	3.6
Effluent	0.02	0.02	1.94	0.003	0.025	0.04	8.9

Results showed that SRB performed best on Zn, Cd, and Cu. At the end of the project, the bioreactors were decommissioned and the site was restored to nearly original condition. Autopsy sampling included collection of solid matrix samples for chemical analyses to determine concentrations of total metals, SO_4^{-2}, S^{-2}, N, P, and total organic carbon (TOC) in the chambers of organic matter and limestone. Bacteriological analyses were also conducted to determine SRB population in the organic substrate and in the limestone. Aqueous samples also were collected from the previously inaccessible bottom of the crushed limestone and cobble chambers and analyzed for total and dissolved metals.

The autopsy on the bioreactors revealed a convoluted biochemical environment that was probably caused by the dramatic change in the ARD chemistry after the first 10 months of operation. The material examined during the autopsy showed the mixed results of processes that were occurring at low pH and a reasonably high load of metals with the subsequent reactions that were characteristic for water of neutral pH laden with much less of the dissolved metals (Zaluski et al., 2003). The abundance of TOC present (20% by weight) in the organic matter chamber at the end of the project demonstrated that the bioreactors would have worked equally efficiently with a much smaller supply of organic C, provided the same residence time of ARD was maintained. Since the organic matter mass inhibits permeability, it is prudent to reduce the ratio of organic C to the permeability enhancing component and have a more permeable medium.

Interpretation of monthly monitoring results combined with the autopsy findings allowed for the formulation of a number of conclusions and recommendations. First, the CCS worked very well in preventing settling of the organic matter and ensuring uniform flow of ARD throughout the entire cross-section of the organic C with no preferential flow paths or channeling. Second, the configuring of the bioreactors to accommodate flow in a horizontal plane (rather than in the vertical direction) was successful. Third, time is required for an SRB population to be established in the bioreactors. Once established and supplied with organic matter, SRB can maintain an active population at temperatures ranging from 2 ^oC to 16 ^oC.

Results showed that only Zn, Cu, and Cd were being removed as sulfides due to SRB activities. Changes in concentrations of Fe, Mn, Al, and As, which do not necessarily precipitate as S^{-2}, seemed to be affected by SRB only in an indirect manner by responding to increased pH caused by SRB activity. Most of the metal sulfides that were formed due to the SRB activity precipitated within the organic matter. The same seems to be true for the rest of the metals that must have formed hydroxides and carbonate compounds.

Integrated Biological Treatment

This passive biological treatment process utilizes SRB along with Mn-oxidizing bacteria (MOB) to neutralize ARD and remove contained dissolved metals. Bench-scale testing was preformed to develop an integrated anaerobic with aerobic system parameters. Anaerobic treatment with SRB is used for As, Cd, Cu, Fe, Pb, and Zn removal. An aerobic treatment is used for Mn oxidation/removal and polishing to remove organics. Figure 3 is a schematic of the process flows through the designed treatment system.

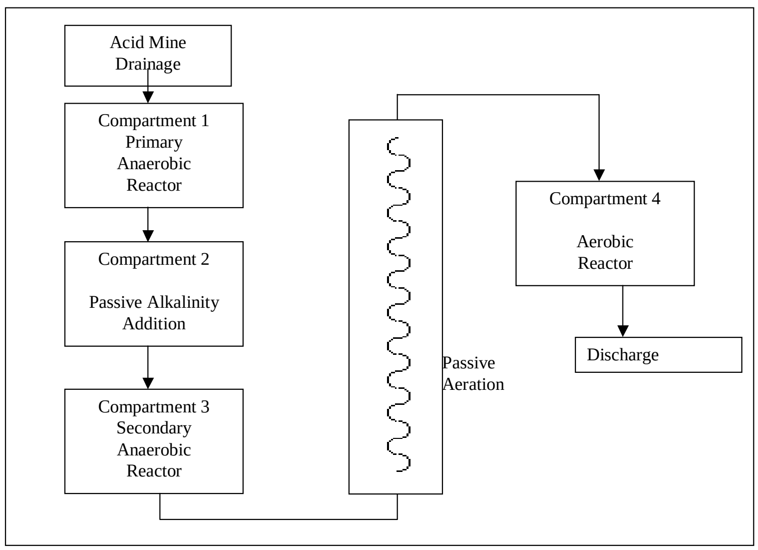


Figure 3. Block-flow of treatment system.

A pilot-scale system of this innovative passive treatment process was installed by MSE to treat ARD at the Surething Mine in Montana. At the demonstration site the bacteria live within a series of pit-type reactors constructed within the waste-rock pad located outside of the mine adit. Flow through the bioreactors is gravity dependent. The goal of this demonstration is to prove that this technology offers a comprehensive passive cleanup method for numerous remote or abandoned mines that discharge acidic metal-contaminated water (Nordwick and Bless, 2002).

The chemical parameters typical to untreated Surething Mine water are shown in Table 3 along with the dissolved metals and the effluent water chemistry for the initial effluent.

Table 3. Typical Sure-thing Mine influent and effluent dissolved metals and pH.

	Iron (mg/L)	Zinc (mg/L)	Aluminum (mg/L)	Manganese (mg/L)	Arsenic (mg/L)	Cadmium (mg/L)	Copper (mg/L)	pH
Feed	15.0	22.7	29.5	26.7	0.13	0.21	2.35	2.5
Effluent	U	U	U	0.04	0.01	U	U	6.9

Note: U is undetected.

Evaluation of the data shows that overall metal removal was extremely high. This is attributed to slow self-establishment of an indigenous MOB population in the final reactor. As the demonstration progressed, design improvements were made and the removal of manganese was increased to present levels.

Improvements in Engineered Bioremediation of ARD

Another MWTP research project involves an investigation to improve the construction of SRB bioreactors. This SRB laboratory-based ARD bioremediation research project had three main objectives:

(1) to develop a bioreactor design with a reactive material not prone to plugging and easy to replace if exhausted,

(2) to develop a bioreactor cartridge system that can be easily transported to ARD sites often difficult to access, and

(3) to quantify reactivity of organic material and develop software that would facilitate optimizing the design parameters and the size of the bioreactor.

To meet the first project objective, a literature study was conducted to develop a database on organic matter used as an electron donor in bioreactors. This database indicated that the best long-term bioreactor performance is achieved using a mixture of substrates with varying degrees of biodegradability. The database indicated that an easily biodegradable substrate is important for the startup of a bioreactor and a substrate with a low biodegradation rate enhances long-term performance. The database also indicated that the loss of permeability of the organic C is a hindrance for the longevity of operation.

With the library of information, a new organic matter was selected as a mix of cow manure and walnut shells. Cow manure was chosen as it is easily biodegradable and contains N as NH_4^+, which is necessary for SRB growth. Walnut shells were chosen due to the high percentage of organic C, which can be up to 60%, and slow biodegradation rate. Walnut shells would serve to enhance the overall long-term bioreactor performance. Due to their shape, walnut shells increase the porosity of the mix and provide an internal structure that prevents settling of the material, thus preserving high permeability of the organic medium.

Both field-scale and bench-scale investigations were conducted on the permeability of the manure and walnut shell medium. It was demonstrated that although the permeability may be controlled by the ratio of walnut shells to manure, it is best preserved with a horizontal flow configuration.

To meet the second project objective, a replaceable cartridge consisting of a 2.44-m (8-ft) diameter tank filled with bags each containing approximately 18.9 L (5-gal) of a mixture of cow manure and walnut shells was proposed. The bags were made of plastic netting with 1.27 cm (0.5-in) openings. Each bag has a loop on the top to be used for lowering it into the tank and to allow for easy bag removal if the organic matter needs to be replaced (Fig. 4 and 5). The tank can be placed below or aboveground. It is fitted with inlet, outlet, and overflow pipes, and it contains large vertical cleanup ports to occasionally remove accumulated sediment and/or precipitated metal sulfides.

The third project objective was to quantify reactivity of organic material and develop software that would facilitate optimizing the design parameters and the size of the bioreactor. An experimental set-up was developed to determine the SO_4^{-2} reduction rate and a routine was defined for using the PHREEQC geochemical model to simulate chemical reactions occurring as flow proceeds through the system. A spreadsheet model was developed to size the bioreactors (Zaluski et al., 2005). This model is called BEST (bioreactor economics, size and time of operation) and is an Excel™ spreadsheet-based model that is used in conjunction with the public domain geochemical modeling software, PHREEQCI. Input variables depend on the concentration of metals in the ARD, the pH of the ARD, sulfate reduction rate, and an assumed rate of organic C depletion.

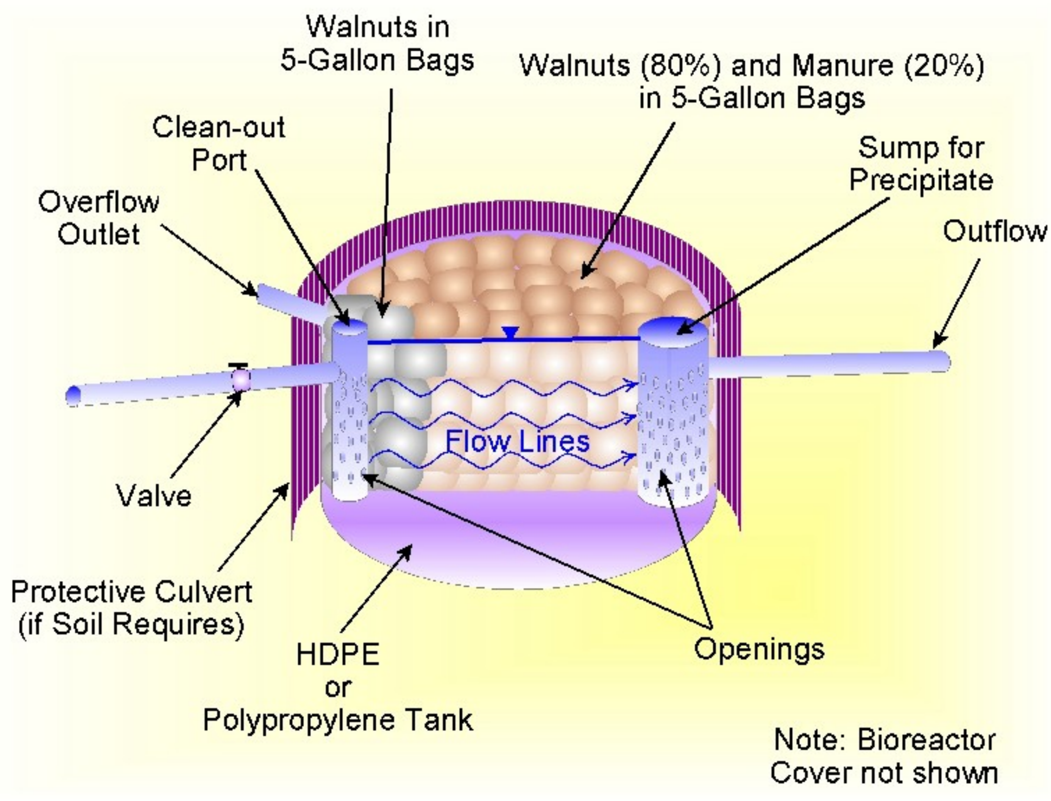
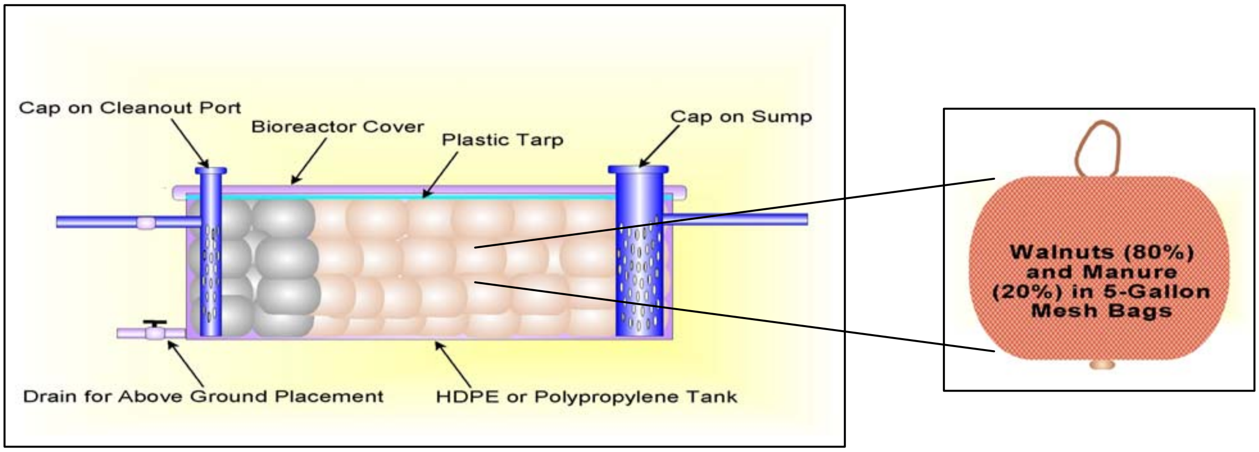


Figure 4. Preliminary design of replaceable cartridge bioreactor system.

Figure 5. Five-gallon plastic mesh bag with organic matter.



Summary

The MWTP has worked to advance the development of SRB technologies to treat ARD. As part of this work, MSE has conducted both bench-scale testing and field demonstrations to demonstrate the benefits of employing SRB technologies to mitigate ARD. The advantages of SRB bioreactors include: the reduction of dissolved metal ions by formation of insoluble metal sulfides, and the neutralization of the ARD from the resultant production of HCO_3^- generated by the oxidation of organic nutrients.

This paper presented summaries of four individual MWTP projects and described the developed designs that have been employed such as the submerged in situ bioreactor at the Lilly Orphan Boy Mine, the SRB on-site bioreactor installed at the Calliope Mine, the integrated biological reactors built at the Surething Mine, and the ongoing development of a replaceable cartridge system. These MWTP demonstrations show that SRB bioreactors are very effective for passive ARD treatment.

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