EPA HardrockMining Innovative Technology Case Study

Leviathan Mine

Compost-Free Sulfate-Reducing Bioreactor Treatment of Aspen Seep

ABSTRACT:

The Leviathan Mine is the former site of intermittent mining operations dating back to the 1860s, and open pit sulfur mining operations from the 1950s through the 1960s. A pilot scale bioreactor was first installed at the Leviathan Creek seep in 1993, and transferred to the Aspen Creek seep in the late 1990s. In 2003, Atlantic Richfield Company and researchers from the University of Nevada-Reno (UNR) and the U.S. Environmental Protection Agency (EPA) installed a full-scale compost-free sulfate-reducing bioreactor system to treat acid rock drainage (ARD). Over an evaluation period of 20 months, from late 2003 to summer 2005, the bioreactor was able to achieve a target-metal removal efficiency of 95 percent. All target metals, except iron, were reduced to concentrations below the EPA interim discharge standards. The compost-free bioreactor system also raised the pH of the ARD from 3.0 to 7.0 and treated influent flows up to 30 gallons per minute (gpm) year-round. This case study looks at the effectiveness of the sulfate-reducing bioreactor treating ARD from the Aspen Seep at Leviathan Mine.

SITE BACKGROUND

Leviathan Mine
CERCLIS ID: CAD98067685

The Leviathan Mine is located in Alpine County, California near the California-Nevada border. The disturbed land comprises approximately 250 acres at the 7,000-foot elevation on the eastern slope of the Sierra Nevada. Mining operations commenced in the 1860s, but the mine was inactive from 1872 to 1935. The mine operated intermittently until the Anaconda Company purchased the property in 1951 and extracted sulfur by open pit mining from 1952 to 1962. No significant mining activities have occurred since Anaconda ceased operations in 1962 and sold the property (U.S. EPA, 2004c).

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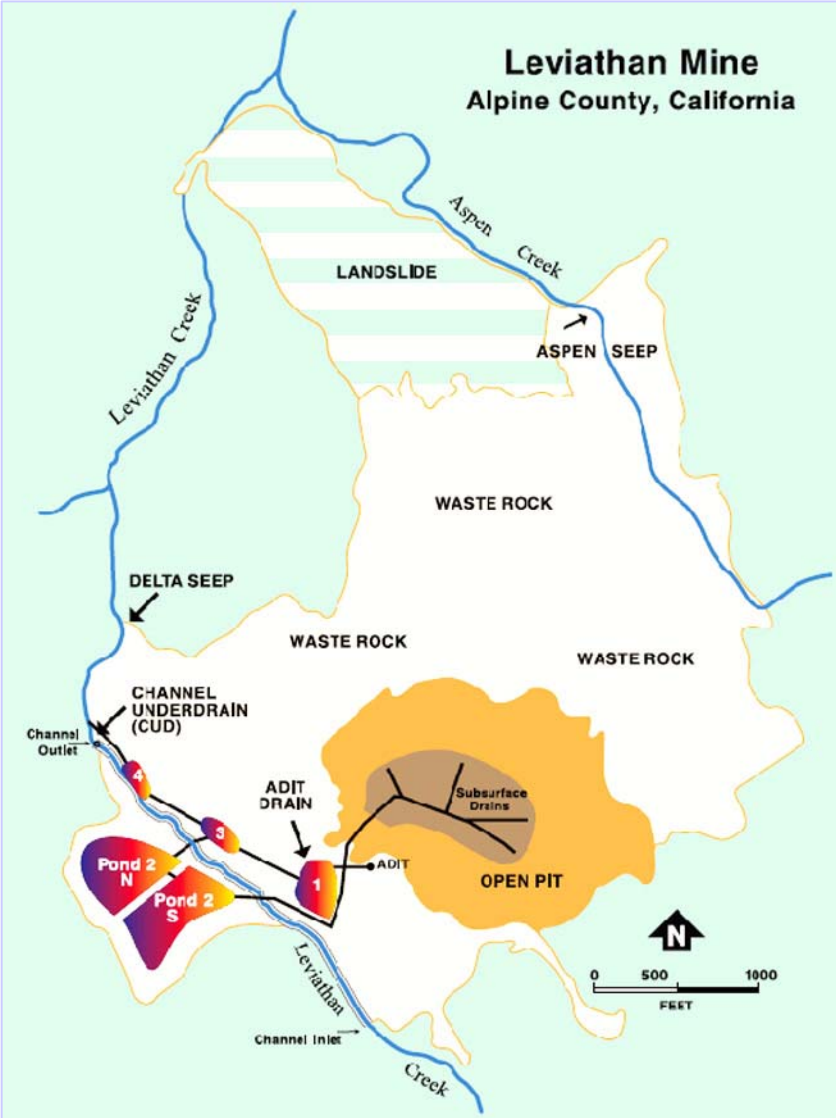

Figure 1: Leviathan Mine Disturbed Area with major known ARD points including Aspen Seep.

(Source: U.S. EPA, 2004a).

Major environmental damage occurred at the mine, which is surrounded by the Humboldt-Toiyabe National Forest, during the period of open pit mining. Snowmelt, rain, and groundwater interact with the waste rock, creating sulfuric acid, which in turn leaches additional contaminants from the native minerals such as arsenic, copper, nickel, zinc, chromium, aluminum and iron. The resulting acid rock drainage (ARD) flows into the Leviathan Creek system at numerous points, eventually joining the East Fork of the Carson River. For most of the year, roughly half of the flow in Leviathan Creek is composed of ARD (U.S. EPA, 2004c).

When the Leviathan Mine was added to the National Priorities List (NPL) in May 2000, EPA identified two problems requiring immediate attention: (1) an evaporation pond, known as Adit Drain, collecting highly contaminated acid drainage, which overflows into the Leviathan Creek during the spring snowmelt; and (2) three seeps of acidic drainage causing contamination to enter Leviathan Creek and Aspen Creek (Figure 1) (U.S. EPA, 2004a). One of these seeps, Aspen Seep, originates from dumped overburden and flows into Aspen Creek. A sulfate-reducing bioreactor (SRB), designed and operated by Atlantic Richfield Company and University of Nevada-Reno (UNR) and EPA researchers, treats the drainage from the Aspen Seep. More traditional lime-based treatment systems are currently being used to treat the other two contamination sources (Delta Seep/Channel Underdrain and Adit Drain) at the Leviathan Mine site. The final, long-term remedy for this site has not been selected. This case study focuses on the effectiveness of the Aspen Seep SRB to date.

WASTE STREAM CHARACTERISTICS

Leviathan Mine was added to the NPL in May 2000 to address contamination of surface water from acid mine drainage (AMD) and ARD. ARD released from the Aspen Seep into Aspen Creek contains elevated levels of four primary metals: aluminum, copper, iron, and nickel. Each of these metals has historically exceeded EPA interim discharge standards by over 500 times. Secondary metals of concern include selenium and zinc. Fish and insect kills in Leviathan Creek, Bryant Creek, and the

East Fork of the Carson River have been attributed to the release of metal-laden ARD. ARD, at pH 3, flows from the Aspen Seep at rates ranging from 8 to 30 gallons per minute (gpm). Table 1 shows average concentrations of these primary metals and the pH prior to treatment and compares the concentrations to the EPA Interim Discharge Standard for Leviathan Mine (U.S. EPA, 2006).

Table 1. Concentrations and EPA Interim Discharge Standards for primary metals in ARD at Aspen Seep

Target Metal	Average Influent Concentration (mg/L)	EPA Interim Discharge Standard (Average, mg/L)
Aluminum	37.5	2.0
Copper	0.690	0.016
Iron	117.0	1.0
Nickel	0.487	0.094
Selenium	0.013	0.005
Zinc	0.71	0.21

TREATMENT TECHNOLOGY

The State of California – site owner and, therefore, partially responsible for cleanup – had funded a bioreactor treatment system at the Leviathan Mine since the early 1990s. The system started as a simple one-cell, pilot-scale bioreactor with a manure substrate. The system continued to evolve throughout the late-90s but did not take its current form until the site was listed on the NPL. After the site became final on the NPL, EPA directed Atlantic Richfield to prevent ARD discharge from the Aspen Seep and several other discharge points. The State of California wanted the bioreactor system to be part of the Atlantic Richfield responsibility for cleanup. Atlantic Richfield saw promise in the system but felt it needed some improvements. The EPA Office of Research and Development (ORD), Atlantic Richfield, the State, and UNR researchers convened for a design session to offer different approaches and ideas for constructing and implementing a full-scale bioreactor treatment system at the site. As a team, they proposed a system design, and the full-scale, compost-free bioreactor system was constructed in 2003. As constructed, the system requires 0.75 acres.

ASPEN SEEP SRB CHEMICAL REACTIONS:

Chemical reaction for sulfate-reducing bacteria using an alcohol carbon source:

$$4AH_2 + SO_4^{2-} + H^+ \rightarrow 4A^{2-} + HS^- + 4H_2O$$
$$H_2S + M^{2+} \rightarrow MS + 2H^+$$

AH_2 is the carbon source and SO_4^{2-} is the terminal electron acceptor in the electron transport chain of the sulfate-reducing bacteria. This causes an increase in pH. H_2S reacts with metals and results in metal sulfide precipitate (MS).

The reduction of sulfate to sulfide:

$$H_2SO_4 + 8H^+ + 8e^- \rightarrow H_2S + 4H_2O$$

Ethanol contributes 12 electrons per molecule oxidized.

$$3H_2O + CH_3OH \rightarrow 12e^- + 2CO_2 + 12H^+$$

Electron counting enables determination of the amount of carbon source required to reduce sulfate.

The bioreactor at the Leviathan Mine Aspen Seep relies on sulfate-reducing microbial organisms, such as *Desulfovibrio* sp., to reduce sulfate to sulfide. These organisms function at a critical pH 4.0 (Tsukamoto and Miller, 2005). ARD from the Aspen Seep has pH 3.1 and, therefore, requires pretreatment before entering the compost-free bioreactor treatment system. In order to accommodate this requirement, a 25 percent sodium hydroxide solution (0.26 ml/L) is added to the influent in a pretreatment pond (1,000 ft^3). The influent is effectively increased to pH 4.0 before it enters the compost-free bioreactor system. Ethanol (0.43 ml/L) is also added to the system to provide a carbon source for the sulfate-reducing microbes (U.S. EPA, 2004b, 2006a, 2006b).

After addition of the sodium hydroxide solution and ethanol, ARD flows to Bioreactor No. 1 to reduce sulfate to sulfide. Bioreactor No. 1 measures 12,500 ft^3 in total volume and 5,300 ft^3 in active volume, with a 22-hour hydraulic residence time (HRT) at 30 gpm. The bioreactor is lined in 60 mil high-density polyethylene (HDPE) and is filled with 6- to 24-inch river rock. Along with supplying a substrate for the bacteria to grow on, the river rock also provides stabile flow paths and allows precipitates to be flushed through the matrix. Sulfide generated in the first bioreactor is passed to the second bioreactor for additional metals removal. With a 13-hour HRT at 30 gpm, Bioreactor No. 2 measures 7,000 ft^3 in total volume and 3,000 ft^3 in active volume (Figure 2). Each bioreactor has three influent distribution lines and three effluent collection lines at different elevations to allow variable flow operations.

Figure 2: Aspen Seep Bioreactor No. 2 lined with HDPE and filled with river rock.
(Source: The photo is courtesy of J. Bauman)

After passing through the bioreactors, a 25 percent sodium hydroxide solution is once again added to the effluent to increase the pH to a neutral condition. A continuous-flow pond, measuring 16,400 ft^3 with a 68-hour HRT at 30 gpm, collects the effluent from the second bioreactor for extended settling of metal sulfide precipitates. The effluent from this settling pond flows over a rock-lined aeration channel, measuring 150 feet long and two feet wide, to promote degassing of residual hydrogen sulfide prior to discharge.

To prevent plugging of the rock matrix, precipitate slurry is flushed occasionally from the bioreactors. The slurry is settled in a flushing pond (18,000 ft^3, 75-hour HRT at 30 gpm). Occasionally, solids are pumped out of the settling and flushing ponds and dewatered using a 10- to 15- foot spun-fabric bag filter. Under California and Federal standards, the bag filter solids are not hazardous.

The total system HRT is 107 hours at maximum design flow of 30 gpm.

MODIFICATIONS TO INITIAL DESIGN

System Design

Although the system has experienced nearly constant tweaking, the following is a description of the three major bioreactor treatment system designs: manure substrate pilot-scale; two-cell bioreactor, and full-scale compost-free.

The original pilot-scale bioreactor developed by the UNR research team in the early 1990s was a simple system consisting of a manure substrate in a small, shallow pond (Tsukamoto and Miller, 2005). This organic substrate served as both the physical structure and the sole carbon source for the sulfate-reducing bacteria. However, once the carbon source was depleted, ARD treatment slowed down. Additionally, ARD from the Leviathan Seep proved too acidic for the sulfate-reducing bacteria to function optimally, further reducing the efficiency of waste stream treatment. The drainage at Leviathan Creek was from waste rock, described as material containing less than 20 percent sulfur by mass. After the first year of operation, the researchers determined the bioreactor was ineffective in treating ARD from the Leviathan Seep.

In order to address problems with the initial bioreactor design, the system experienced a facelift in 1998 (Tsukamoto and Miller, 2005). A new two-cell bioreactor was constructed at the Leviathan Mine Aspen Seep. The ARD from the Aspen Seep, originating from dumped overburden, is a less acidic waste stream and enabled the microbes to have a better chance of survival. In addition to the location, key modifications implemented in the 1998 bioreactor included:

- Developing a two-cell system utilizing wood chips and an inert rock matrix,
- Employing alcohol as a carbon source,
- Adding base to further increase the alkalinity of the ARD, and
- Allowing precipitates to be flushed from the bioreactor cells.

The use of alcohol as a carbon source provides an advantage over other organic substrates. Alcohol can be used for treatment over extended time periods, and it also maintains a liquid state under varying environmental temperatures. Finally, the addition of alcohol to a treatment system can be varied according to optimal operating conditions. Alcohol, specifically ethanol, is an ideal substrate for use at the Leviathan Mine Aspen Seep due to the remote nature of the site as it is only accessible for a few months out of the year.

Again in 2003, the system was redesigned and the compost-free bioreactor treatment system was constructed. The most recent design of the bioreactor uses a rock matrix in both bioreactor cells, includes a pretreatment pond, and has improved flow distribution and advanced sludge capture capability.

Operation Mode: Gravity-flow vs. Recirculation

Over the first six months of evaluation, the 2003 bioreactor design operated under gravity-flow mode (Attachment A). Gravity-flow mode allowed metal precipitates to accumulate in both the bioreactors and the settling pond. This required the system operators to flush the system frequently, in turn disturbing the bacteria in the bioreactors. In order to avoid the need to flush the system so frequently, the researchers transferred the system into recirculation mode for the remaining 14 months of the evaluation period (Attachment B). In recirculation mode, untreated ARD is mixed with a 25 percent sodium hydroxide solution and sulfide-rich water from Bioreactor No. 2. The mixture then flows into the settling pond where the high pH and high sulfide concentrations encourage precipitation of metal sulfides. This prevents the metals sulfides from precipitating in the bioreactors. The pH of the water moving through the bioreactors is nearly neutral, presenting ideal conditions for the sulfate-reducing bacteria. The system required 17 percent less sodium hydroxide while operating under recirculation mode (U.S. EPA, 2006b).

PERFORMANCE OF SYSTEM

Compost-free Bioreactor

The 2003 compost-free bioreactor was evaluated between November 2003 and July 2005 as part of the Superfund Innovative Technology Evaluation (SITE) program. This effort was possible through the cooperation of the U.S. EPA National Risk Management Research Laboratory (NRMRL), EPA Region IX, the State of California, Atlantic Richfield, and UNR (U.S. EPA, 2006b).

Table 2. Bioreactor Treatment System Removal (U.S. EPA, 2006b)

Full-scale Compost-free Bioreactor					
	Gravity-flow Mode (11/2003 – 4/2004)		Recirculation Mode (5/2004 – 7/2005)		
	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)	EPA Interim Discharge Standard (mg/L)
pH	3.1	7.2	2.9	7.6	--
Al	37.5	0.1	40	0.05	2.0
Fe	117	4.9	116	2.7	1.0
Ni	0.49	0.07	0.53	0.07	0.094
Cu	0.69	0.005	0.79	0.005	0.016
Sulfate	1502	1222	1530	1170	--

The system achieved an increase in waste stream pH from 3.0 to over 7.0 during treatment (Table 2). Additionally, although the influent concentrations of the target metals were up to 580 -fold greater than EPA interim standards, effluent concentrations were up to 43 fold below the standards. The system was also able to reduce the sulfate concentration in ARD by more than 17 percent.

During the first six months of evaluation, while the system operated in gravity-flow mode, 2.44 million gallons of ARD was treated. The system utilized 2,440 gallons of sodium hydroxide solution and 1,180 gallons of ethanol. Removal efficiency of target metals exceeded 94 percent.

Over the following 14 months, while the system functioned in recirculation mode, over 5.8 million gallons of ARD was treated achieving a removal efficiency of target metals exceeding 96 percent. During this time, 5,280 gallons of sodium hydroxide and 2,805 gallons of ethanol were pumped into the system.

The system operates year-round and treats up to 30 gpm in either mode.

LESSONS LEARNED

A bioreactor treatment system, ranging from pilot-scale to full-scale implementation, has been operating at the Leviathan Mine since 1993. The technology has experienced many changes since its inception. In its current form, this treatment technology operates year-round and is compliant with EPA discharge standards for all target metals except iron.

As the site remedial project manager explains, initially designed with simplicity in mind, the Aspen Seep SRB has required more operator involvement than originally anticipated because pumping is required to keep the system operating properly. Although the system has proven to be both effective and reliable, it has also required more maintenance than originally planned.

The remote nature of the site and the surrounding environment are impacting system operations. The climate is also influencing the system with slower biological activity during the winter months. Winter snowpack limits access to the site for eight months out of the year requiring operating materials such as sodium hydroxide, ethanol, and diesel fuel to be stored in bulk before the winter. Similarly, equipment replacement, sludge dewatering, and sludge transfer are all performed during the summer months (U.S. EPA, 2006a).

This technology can now be implemented at other sites. Initiating the technology on a pilot scale, the 2006 Technology News and Trends explains, is no longer necessary. The bioreactor system at Leviathan Mine successfully addressed problems related to carbon availability and sulfate reduction. However, due to the unique characteristics of each site, the dose for base and ethanol would need to be determined through a simple bench test (U.S. EPA, 2006b).

COST

The capitol costs for construction of the gravity-flow operation amounted to $836,600 and changing to the recirculation mode added nearly $30,000, for a total of $864,100. Operating at an average flow rate of 10 gpm, the operation and maintenance costs of the system are $15.73 per 1,000 gallons of treated ARD (U.S. EPA, 2006b).

KEY DATES

(U.S. EPA 2001; 2004a, b, c; 2006a, b)

Early 1960s	The California Regional Water Quality control Board, Lahontan Region (Regional Board) become involved at the site.
Early 1980s	The California Regional Water Quality control Board, Lahontan Region (Regional Board) negotiate a settlement with Atlantic Richfield Company (corporate successor to Anaconda).
1984	The State of California purchases the property to address the contamination.
1993	Pilot-scale Bioreactor begins to treat AMD at Leviathan Creek Seep.
1997	Washoe Tribe in Nevada and California requests EPA's involvement at the site.
1998	Researchers from the University of Nevada-Reno install a two-cell bioreactor at Aspen Seep.
2000	Leviathan Mine is listed on the NPL.
2001	Aspen Seep bioreactor treats over 2.5 million gallons of ARD.
2003	Atlantic Richfield and UNR install a full-scale, compost-free bioreactor system at Aspen Seep. The bioreactor treats over 5.0 million gallons of ARD. NRMRL initiates long-term evaluation of the bioreactor.
2005	NRMRL completes long-term evaluation of SRB system.

The compost-free sulfate-reducing bioreactor at the Aspen Seep is the first of its kind. The project was labor intensive because the operating conditions at the site were continually altered to stress and test the system. The system also included many optional features, such as controlling and routing flows, that would not normally be used in most systems. Because of these factors, the final costs are likely to be higher at Leviathan than the cost of operating and maintaining the system at other sites.

EPA CONTACTS

Kevin Mayer
Remedial Project Manager
U.S. Environmental Protection Agency Region IX
Phone: (415) 972-3176
Email: Mayer.Kevin@epa.gov

Edward Bates
Project Manager
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Office of Research and Development
Phone: (513) 569-7774
Email: Bates.Edward@epa.gov

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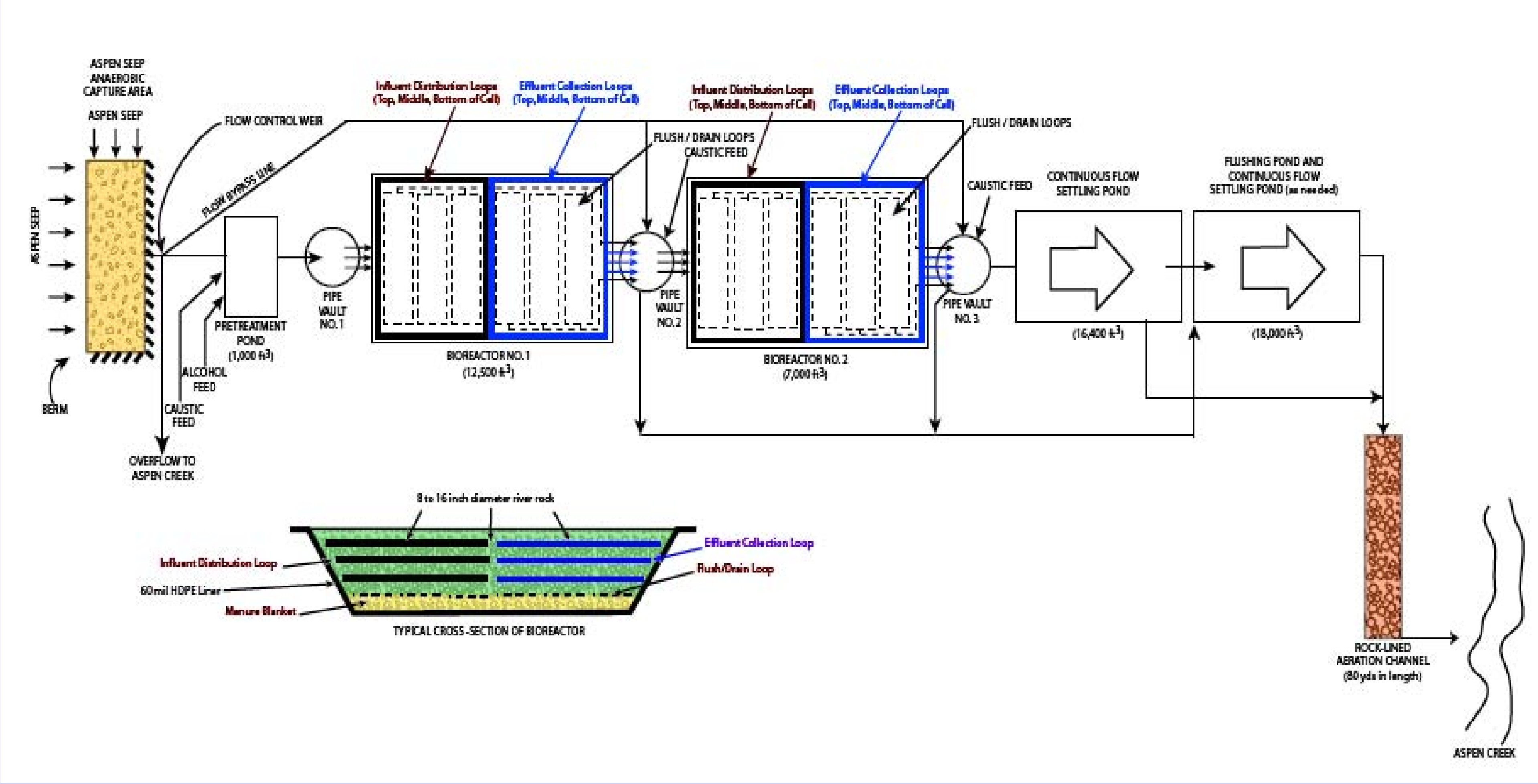
ATTACHMENT A: SRB SYSTEM OPERATIONS IN GRAVITY-FLOW MODE (U.S. EPA, 2006B)



ATTACHMENT B: SRB SYSTEM OPERATING IN RECIRCULATION MODE (U.S. EPA, 2006B)