LOW-PH IRON REMOVAL AS PART OF MULTI-STAGE PASSIVE TREATMENT[1]

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Abstract. Through a contract with the US Army Corps of Engineers, Baltimore District, an innovative passive system to treat drainage from an abandoned underground coal mine was completed in 2008. The discharges can be characterized as highly acidic (pH 2.7, 1400 mg/L acidity) with moderate to high metal concentrations, having average total iron, manganese, and aluminum values of 300 mg/L, 20 mg/L, and 140 mg/L, respectively. The passive system utilizes a variety of treatment components including mixed-media vertical flow ponds, an anoxic limestone drain, a horizontal flow limestone bed, settling ponds, wetlands, etc. Of particular interest is the use of oxidation and precipitation channels to form iron solids at low pH. Preliminary results indicate that on average about 230 mg/L of dissolved iron is being removed at 2.6-3.2 pH. Removal of iron within the channels is expected to decrease operation & maintenance requirements while increasing the overall life of the system. Other design considerations included decreasing the potential for saturation with respect to gypsum, increasing alkalinity through anaerobic decomposition and sulfate reduction in alkaline mine drainage sources, and creating elk habitat. The final system effluent is net alkaline (7.5 pH, 214 mg/L alkalinity, -180 mg/L acidity) with total iron and aluminum less than 1 mg/L and total manganese of about 5 mg/L.

Additional Key Words: AMD, ferrous iron oxidation, oxidation precipitation channels

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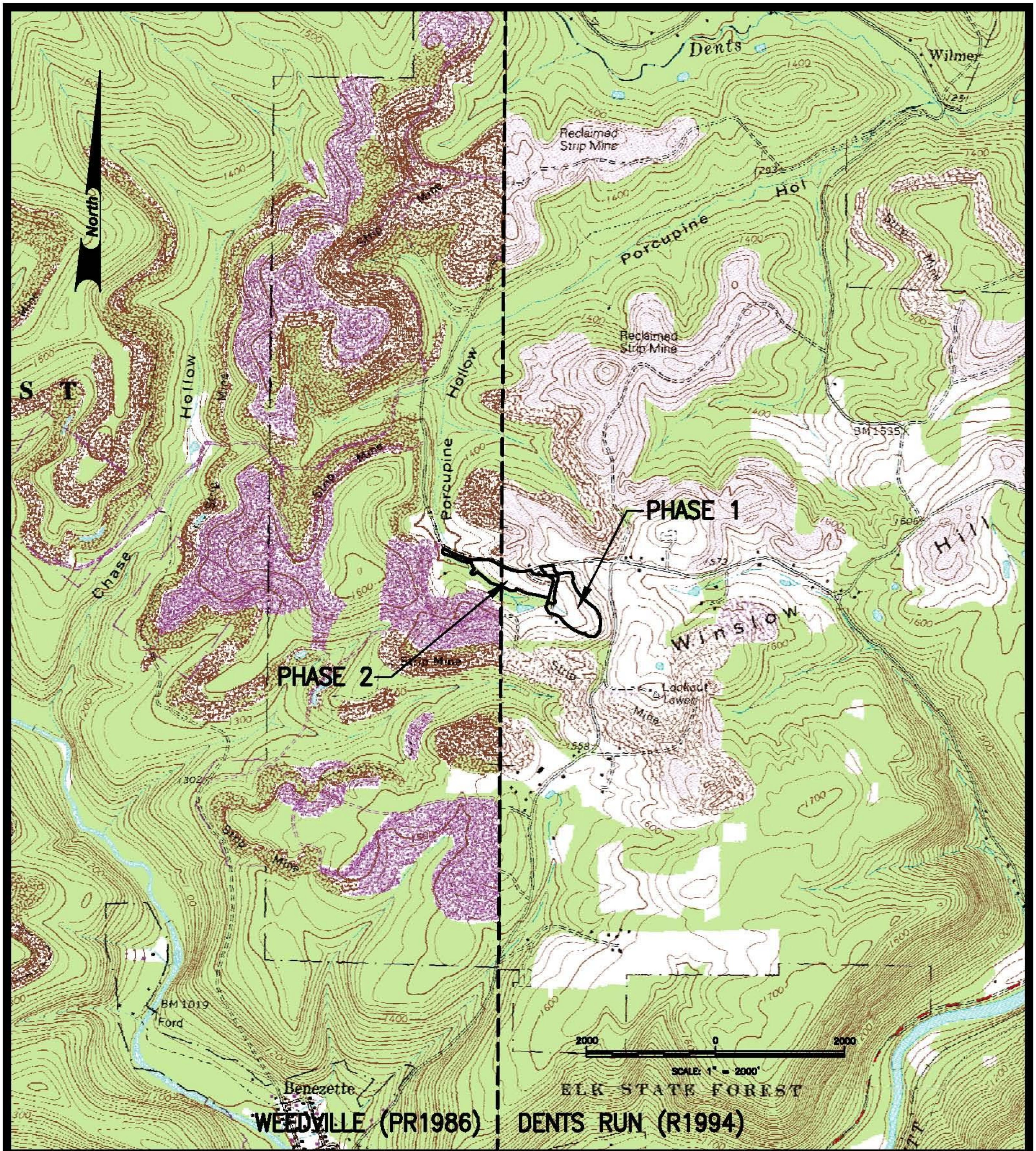
Introduction

Coal mining activities have been conducted within the 6,600-ha (25.5-square mile) Dents Run Watershed since the late 1800s. Degraded mine drainage from abandoned underground workings, unreclaimed spoil, and coal refuse piles severely impact the watershed. A public-private partnership effort has been spearheaded by the Bennett Branch Watershed Association and the Elk County Conservation District in cooperation with the US Army Corps of Engineers (USACE) Baltimore District, the Pennsylvania Department of Environmental Protection Bureau of Abandoned Mine Reclamation (BAMR), the Pennsylvania Game Commission and various consulting, mining, and construction companies to restore Dents Run. Located in the headwaters of the Chesapeake Bay, Dents Run is classified as a High Quality Cold Water Fishery and is a tributary of the Bennett Branch of Sinnemahoning Creek within the West Branch Susquehanna River Watershed. According to the "Dents Run Watershed, Elk County, PA: Final Detailed Project Report and Integrated Environmental Impact Statement" (USACE, 2001):

> "The primary source of AMD to Dents Run is from abandoned coal mines along Porcupine Hollow…Because [the drainage from the 1700-acre] Porcupine Hollow is so severely degraded, the water quality… at the confluence with Dents Run drops from [a pH of] ~6.0 above, to less than 3.5 below the confluence… The effect of the AMD from Porcupine Hollow on Dents Run is dramatic and devastating to the ecosystem. In addition to the degraded aquatic habitat …terrestrial and riparian habitat along Dents Run and Porcupine Hollow are severely impacted…"

Dents Run, after receiving drainage from Porcupine Hollow, is essentially devoid of life while the non-impacted upper portion has a healthy ecosystem supporting native trout (USACE, 2001).

The USACE Baltimore District retained BioMost, Inc. to design a passive treatment system in order to abate the highly acidic, metal-bearing, discharges associated with an abandoned underground coal mine in Problem Area 3895 in the headwaters of Porcupine Hollow. Site 3895 is located in Benezette Township, Elk County, PA at 41° 20' 24" latitude and 78° 22' 15" longitude on the 7½' USGS Dents Run (PR1994) and Weedville (PR1986) topographic maps on PA State Game Lands No. 311 and Nye et al property (See Figure 1.). The site can be accessed from Dewey Road (T-445).



DENTS RUN SITE 3695 - PHASE 2
SECTION 206, ACID MINE DRAINAGE
BENEZETTE TOWNSHIP, ELK COUNTY, PA
USACE Contract W912DR-04-D-0007, DO 0003

USGS 7.5' DENTS RUN & WEEDVILLE
TOPOGRAPHIC MAP (PORTION)

U.S. ARMY ENGINEER DISTRICT, BALTIMORE CORPS OF ENGINEERS BALTIMORE, MARYLAND	Designed by: TPD		Date: AUGUST 2007
	Dwn By: SLB	Ckd by: CFD	Design file no. 1622 100 PERCENT
BioMost, Inc. Mining and Reclamation Services 3016 Unionville Road Cranberry Township, PA 16066 (724) 776-0161	Reviewed by: MHD		Drawing number:
	Submitted by: BIOMOST, INC.		File name: Plot date: Plot Scale: 1" = 2000'

Figure 1. Location Map

The approximately 40-ha (100-acre) headwaters of Porcupine Hollow has been extensively mined by both underground and surface methods to recover bituminous coal (Pennsylvanian Allegheny Gp.; Kittanning Fm.). Based on the sulfate content of the various water sources that were sampled, a limited site investigation, aerial photography, and review of mine permit boundaries, the majority of contributory drainage to "Porcupine Run" appears to issue from, flow through, and/or intercept drainage from areas disturbed by coal extraction activities. The abandoned mine drainage at Problem Area 3895 represents ~6% of the total acid load in Dents Run and the discharges of concern emanate from abandoned underground mine workings in an area referred to as Phase 1 (USACE, 2001). Abandoned coal refuse, estimated at ~1500 cubic meters (~2000 cubic yards) later revised to ~3800 cubic meters (~5,000 cubic yards) (BioMost, 2007) also impacted "Porcupine Run".

Water Quality Characterization of Site Drainage

Two collapsed drift entries in the uppermost headwaters of "Porcupine Run" discharge acidic water (sample points 162-2 and 162-3). Pre-construction monitoring of the site was conducted by BAMR from August 1993 through March 1999. Even though the drainage at 162-2 differs somewhat in quality and quantity compared to 162-3, the discharges are relatively similar. All monitoring indicates that the discharges can be characterized as perennial and highly acidic having high concentrations of iron, aluminum, and sulfates with moderate manganese content as identified in Table 1.

Table 1. Water Quality Characteristics of Abandoned Mine Discharges 162-2 and 162-3

Sample Point	Flow	pH	Alkalinity	Acidity	Fe^{+2}	Fe		Al		Mn		SC	SO4
						T	D	T	D	T	D		
162-2	19	2.46	0	2251	98	438	384	152	134	22	17	4296	2411
162-3	38	2.60	0	1658	106	317	240	113	80	21	17	3287	2107

Average values (n=24-26); flow in Lpm; concentrations in mg/L; specific conductivity (SC) in umhos/cm; T-total; D-dissolved (ref: www.datashed.org)

During the design phase, the water monitoring program was expanded to identify and characterize (See Table 2.) other sources of drainage, including net alkaline seeps and discharges to aid in evaluating passive treatment options. All sources sampled had sulfate concentrations

>100 mg/L, indicating that all or a portion of the contributory flow was hydrologically-related to previous mining activities. Seeps/discharges 162-6, 162-8, and 162-10, emanating below surface mining activities in the Phase 1 area, have significant alkalinity and comparatively low metal (Fe, Mn, Al) concentrations. This is probably related to several factors associated with the surface mine operation including the presence of calcareous overburden and/or the incorporation of alkaline material in the recharge area during reclamation, regrading to approximate original contour, and successful revegetation.

Table 2. Water Quality Characteristics of Net Alkaline Seeps and Discharges

Sample Point	Flow	pH	Alkalinity	Acidity	Fe		Al		Mn		SC	SO4
					T	D	T	D	T	D		
162-6	23	6.54	133	-75	3.1	2.6	0.3	<0.1	0.5	0.7	1896	1540
162-8	15	6.79	124	-71	10.0	9.8	1.3	<0.1	0.6	0.6	566	266
162-10	148	6.58	263	-118	1.3	0.2	21.6	<0.1	1.8	1.8	2261	1297

Average values (n=3); flow in Lpm; concentrations in mg/L; specific conductivity (SC) in umhos/cm; T-total; D-dissolved

In addition, a number of other degraded seeps/discharges such as 162-13 and 162-14 (See Table 3.) were identified and characterized during the site investigations. These discharges, although impacting "Porcupine Run", were outside of the project area and could not be incorporated into the passive treatment system.

Table 3. Water Quality Characteristics of Acidic Seeps 162-13 and 162-14

Sample Point	Flow	pH	Alkalinity	Acidity	Fe		Al		Mn		SC	SO4
					T	D	T	D	T	D		
162-13	19	4.01	0	97	1.1	0.6	7.4	6.7	30.9	30.2	1955	1129
162-14	15	3.22	0	302	25.0	24.5	28.2	25.9	51.8	50.6	2769	2162

Average values (n=3); flow in Lpm; concentrations in mg/L; specific conductivity (SC) in umhos/cm; T-total; D-dissolved

Impact of Mine Drainage to Receiving Stream

Prior to installation of the passive system, acidic mine discharges 162-2 and 162-3 formed the headwaters of "Porcupine Run". The net alkaline discharges 162-8, 162-6 and 162-10 entered "Porcupine Run" above sampling point 162-22, which is located about 210 meters (700 feet) downstream at a cross drain (culvert) for a private access road. Downstream of the cross drain, additional springs, seeps, and degraded mine discharges, such as 162-13 and 162-14, enter "Porcupine Run". These discharges further impacted "Porcupine Run" as evidenced at the downstream sampling point 162-21 located at a public road crossing about 780 meters (2,600 feet) downstream of the headwaters discharges 162-2 and 162-3. As depicted in Table 4, "Porcupine Run" was severely degraded prior to the installation of the passive system.

Table 4. "Porcupine Run" Prior to Construction of the Passive Treatment System

Sample Point	Flow	pH	Alkalinity	Acidity	Fe	Al	Mn	Cond.	SO4
162-22	163	3.77	0	597	73.0	45.9	16.2	2202	1342
162-21	261	3.03	0	498	50.6	26.5	21.1	1957	1337

Average values (n=16-54); flow in Lpm; concentrations in mg/L; specific conductivity (SC) in umhos/cm; total metal values (ref: www.datashed.org)

Design Considerations

During the design phase of the Dents Run PA 3895 passive system, a variety of factors were taken into consideration in order to provide effective, long-term, low maintenance treatment of the mine discharges while conforming to the land use of elk habitat.

Enhancing Naturally-Occurring Iron Removal at Low pH

At the 3895 site, iron removal was noted to be occurring naturally at low pH during pre-design investigations. This phenomenon had been previously described by project partner, Tiff Hilton, WOPEC, at a coal mine site in West Virginia, where a natural decrease of 50-60% in total and dissolved iron concentrations and a 35-45% decrease in acidity occurred at a low pH over a 189-meter (600-foot) long channel. He also projected that by treating the water with a chemical treatment system at the end of the channel as opposed to treating the water at the point of issuance would result in using 70% less sodium hydroxide per gallon of AMD treated and produce 35-50% less sludge (Hilton, 2005).

Nonetheless, previous experience at other sites indicated that the iron-bearing material forming at low pH had caused operation and maintenance concerns for passive systems such as, plugged pipes and the apparent decrease in treatment media permeability due to surface accumulations of the iron-bearing material (Denholm, et al, 2006). For instance, the De Sale Phase 1 passive system installed in 2000 in the Slippery Rock Creek Watershed, Butler County, PA treats an acidic mine discharge emanating from an abandoned Middle Kittanning coal surface mine (Pennsylvanian Allegheny Gp.; Kittanning Fm.) with an average total iron, aluminum, and manganese of 80 mg/L, 12 mg/L, 55 mg/L, respectively. Within a year of being placed on-line, however, the concrete flow splitter box installed to divide the raw water between two vertical flow ponds (VFPs) operating in parallel, contained a significant accumulation of hard, dense, iron-bearing material. Removal of the "crusty" iron material from the flow splitter box was required and "snaking or rodding" of the 15.2-cm (6-inch) pipes conveying the flow to the VFPs was required every 3 to 6 months to prevent blockage. To address this issue at De Sale Phase 1, a shallow Forebay with 15.2-cm (6-inch) PVC straight pipes installed at opposite ends to convey the flow to each VFP was installed to receive drainage from the flow splitter box while allowing for the precipitation of iron at a low pH to occur (See Figure 2.). As the flow splitter box discharges to the approximate center of the Forebay, the effective length of the Forebay for each VFP is only about 30 meters (100 feet). Within this limited distance, however, the observed decreases in total iron concentrations have ranged from 20% to 90% without the use of chemicals or treatment media (Denholm et al, 2006). The average total iron influent values to the northern and southern VFPs are 31 mg/L and 51 mg/L, respectively. (View sample analyses at www.datashed.org.)

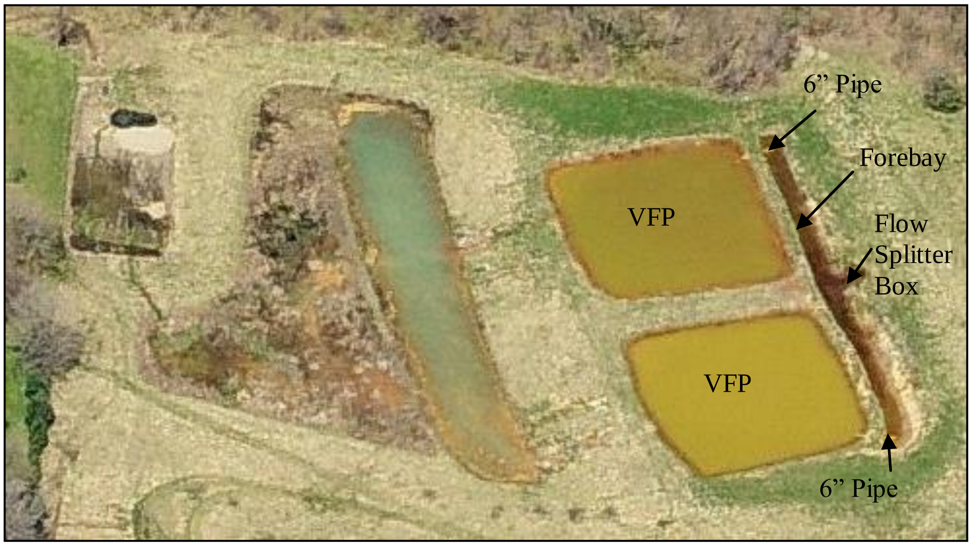


Figure 2. "Aerial View" of De Sale Phase 1 Passive Treatment System showing removal of iron at low pH

Based on the field observations at Site 3895 and with an interest in solving known operation and maintenance issues, the system design was to include component(s) that intentionally promoted the formation and retention of iron solids at a low pH, prior to directing the mine drainage into an alkalinity-generating component.

Enhancing and Utilizing Existing Sources of Net Alkaline Water

To further decrease both long-term treatment and operation and maintenance costs, as discharges 162-2 and 162-3 were so extremely acidic (~2000 mg/L hot acidity), a decision was made to enhance and utilize the existing alkaline mine discharges.

For example, as iron removal at low pH visually appeared to improve after the confluence with the 162-8 net alkaline seep even though little change was noted in pH, this seepage was to be intercepted within a small anoxic limestone drain (ALD) in order to generate some additional alkalinity to possibly enhance low-pH iron removal.

Also, as alkaline discharges 162-6 and 162-10 had relatively low concentrations of iron and were net alkaline, these discharges and other small seeps were to be collected and then directed into a VFP containing an organic mixture of compost and wood chips primarily to increase alkalinity through sulfate reduction and anaerobic decomposition. The effluent of the VFP was then to be introduced into the acidic drainage.

Inhibiting Gypsum Formation

As the sulfate concentration in the discharges was high (>2000 mg/L) and as research had indicated that gypsum may be a contributor to plugging or fouling (decrease in permeability) of treatment media (Rose, et al, 2007), there was concern about saturation with respect to gypsum with the use of limestone as an alkalinity generator. Several design features, therefore, were included at different locations within the system to try to reduce the likelihood of gypsum precipitation. For instance, one of the functions of the organic-only VFP was to decrease sulfate concentrations of the net alkaline mine water through microbial sulfate reduction. Additional decreases in sulfate concentration were also anticipated through the use of a second, mixed media, VFP.

Researchers had also indicated that limestone dissolution may be inhibited and permeability may be decreased with the filling of void spaces in the limestone aggregate by the growth of gypsum crystals (epitaxial nucleation on calcite) (Rimstidt, 2006). The same research also indicated that this process, however, does not occur or is significantly limited with the use of dolomite. As generating alkalinity from magnesium carbonate also decreases the amount of dissolved calcium in the water when compared to the use of a higher calcium carbonate aggregate, saturation with respect to gypsum is further discouraged. On the other hand, the slower dissolution rate for dolomite was a concern. The second vertical flow pond, VFP2B, therefore, was designed to contain a mixture of compost, wood chips, and both limestone and dolomite aggregate. The compost and wood chips were to be used to create reducing conditions to encourage microbial sulfate-reduction, resulting in increased alkalinity and decreased sulfate concentrations.

Creating Elk-Friendly Habitat

As previously mentioned, the project is primarily located on Pennsylvania State Game Lands #311 in Benezette Township, Elk County, which has a thriving elk population making the area a popular tourist destination for this relatively remote section of north-central Pennsylvania. The passive system, therefore, was designed to include some elk-friendly features including gently sloping embankments to enable elk to walk through the system components, vegetative cover in the upland areas for elk browsing, and a pull-off/viewing area for the public.

Passive Treatment System Overview

The Dents Run 3895 Passive Treatment System (See Figure 3.) was designed and installed in two separate phases to incorporate not only most of the seeps, springs, and discharges into a multi-component system, but also to utilize and enhance the pre-existing naturally-occurring processes.

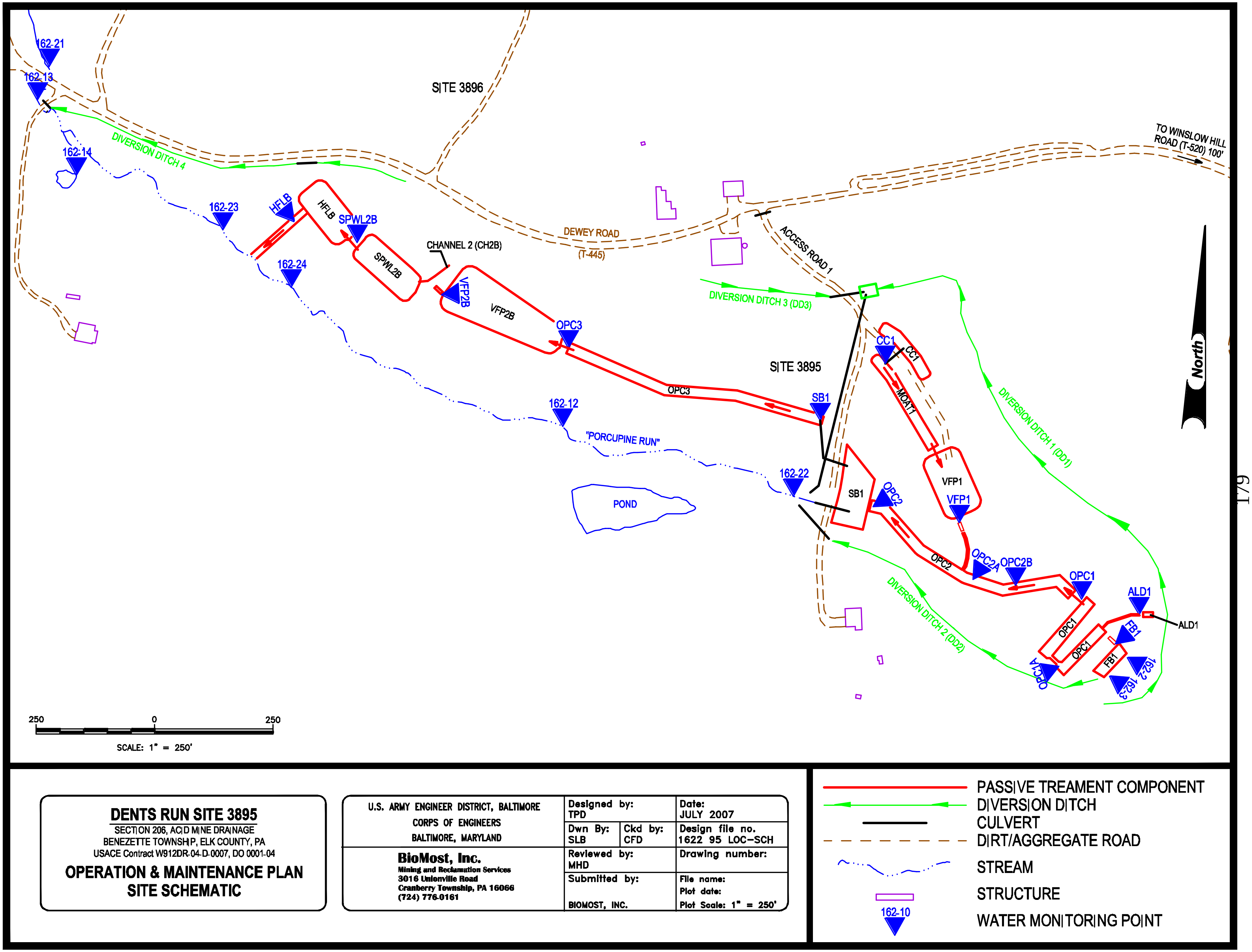


Figure 3. Site Schematic

The first phase consisted of collecting the 162-2 and 162-3 discharges within a Forebay (FB1) which also provides for settling of solids, leaf litter, woody debris, etc. The water then cascades through a Step Aerator (SA1) to provide aeration, to degas carbon dioxide, and to convey the flow into the beginning of Oxidation Precipitation Channel 1 (OPC1) for the purpose of encouraging the formation of iron solids at a low pH. The low-flow, net alkaline seep 162-8 was captured within a small Anoxic Limestone Drain (ALD1) consisting of about 90 metric tons (100 short tons) of $\geq$90% $CaCO_3$ AASHTO #57 (37.5mm x 2.36mm) limestone aggregate to increase alkalinity before discharging into OPC1. As previously noted prior to construction, below the confluence of 162-8 with the acidic mine drainage there visually appeared to be an increased accumulation of iron-bearing solids. The purpose of the ALD was to enhance this process. The combined waters are conveyed in the broad, flat-bottomed, channel, lined with a calcareous (~70% $CaCO_3$) riprap. The OPC was designed to be broad in order to encourage shallow flow and to increase the surface area of the substrate. OPC1 flows into OPC2. At an approximate midway point in OPC2, a different source of net alkaline water enters the flow. The net alkaline discharges 162-6 and 162-10 were intercepted by Collection Channel 1 (CC1) and conveyed into Moat 1 which receives additional seepage and then flows into Vertical Flow Pond 1 (VFP1). The treatment media of VFP1 consists of 765 cubic meters (1000 cubic yards) of an organic mixture with a ratio of 1:1 by volume of spent mushroom compost and wood chips. As discharges 162-6 and 162-10 were net alkaline with relatively low concentrations of metals and high sulfates, the purpose of VFP1 was to generate additional alkalinity through organic decomposition processes and microbial sulfate reduction. The effluent of VFP1 then cascades down Step Aerator 2 (SA2) to degas hydrogen sulfide and carbon dioxide as well as provide aeration before entering OPC2. In OPC2, the two waters mix. As the reduced (negative ORP) net alkaline effluent from VFP1 mixes with the oxidized acidic mine discharges in the remaining section of OPC2, interesting chemical reactions occur including the precipitation of aluminum, precipitation of iron at both low and circum-neutral pH, and what appears to be the precipitation of iron sulfides (See Figure 4.). At the end of OPC2, the combined waters flow into Settling Basin 1 (SB1) which provides settling of metal solids and conveys the water from Phase 1 to Phase 2 via a culvert.

Figure 4. Iron solids forming at low pH (Left), circum-neutral pH (Center), and as iron sulfide (Right) as the VFP1 effluent enters OPC2 at the right the photo

From the culvert, the water enters Oxidation and Precipitation Channel 3 (OPC 3) which was designed to convey the flow to Vertical Flow Pond 2B (VFP2B) and to encourage additional removal of iron at low pH if biogeochemical conditions allowed. VFP2B has a mixed treatment media consisting of 1800 metric tons (2,000 short tons) limestone/dolomite mixed with 1150 cubic meters (1,500 cubic yards) of a 1:1 by volume compost/wood chips mixture. The purpose of VFP2B is to generate additional alkalinity and to remove aluminum remaining in the water. At the effluent of VFP2B, the water cascades down Step Aerator 3 (SA3) to degas hydrogen sulfide and carbon dioxide as well as provide aeration before entering Settling Pond/Wetland 2B (SPWL2B) for the oxidation, precipitation, and settling of any remaining iron as amorphous solids. From SPWL2B, the water enters the final component of the passive treatment system which is the Horizontal Flow Limestone Bed (HFLB). The HFLB was designed to remove manganese as well as increase alkalinity in the final effluent to assist in ameliorating the impact of other AMD discharges that enter “Porcupine Run” downstream of the system effluent.

Passive Treatment System Performance

Construction of Phase 1, which included all passive components except for OPC3, VFP2B, SPWL2B, and the HFLB was completed in 2006. Several monitoring events post-construction of Phase 1 were conducted prior to completion of the design for Phase 2. Phase 2 construction was completed in 2008. Four quarterly monitoring events of the entire system (Phases 1 & 2) were completed in 2009. Table 5 provides current preliminary average results for the individual passive system components. The complete data set for the individual sampling dates is available for viewing and for download at www.datashed.org.

As can be seen from Table 5, the passive treatment system has been successfully treating the abandoned mine discharges. The final effluent of the system which discharges from the HFLB can be characterized as circum-neutral, net alkaline water with very low concentrations of dissolved iron and aluminum and low to moderate concentrations of manganese. Based on available data, the system is, on average, treating approximately 76,000,000 liters (20,000,000 gallons) of mine drainage per year and removing 3,000 Kg (6,700 lbs) of iron and 1400 Kg (3,000 lbs) of aluminum per year.

Interestingly, manganese shows a slight increase in loading of about 1.1 Kg (2.5 pounds) per day even though the final discharge is typically half of the initial concentrations indicating contributions from additional sources. Flow rates do increase within the system especially after VFP1 enters the main flow; however, this contribution typically contains <1 mg/L manganese. As can be seen in Table 5, the average flow rates of the influents to the system (FB1, ALD1, and VFP1) are significantly less than the flow rate of the final effluent (HFLB). While the HFLB average flow is skewed by a rainfall event that had just ended prior to sampling on 9/28/09, there is still indication that the system may be encountering additional manganese-bearing water. Nonetheless, manganese concentrations have not decreased as much as expected. This may be due to the reducing conditions created by VFP2B. Despite the quick reintroduction of oxygen into the water via the Step Aerator (DO >7 mg/L) and the exposure to the atmosphere, both the HFLB influent and effluent often have a negative oxidation-reduction potential (ORP).

Table 5. Performance of Dents Run PA 3895 Passive System & Individual Components

Sample Site	Flow	pH	DO	ORP	T	Acid.	Alk.		Fe		Al		Mn		Ca		SO4
		Field					Field	Lab	T	D	T	D	T	D	T	D	
FB1	19	2.68	5	512	12	1383	0	0	306.0	279.4	136.2	114.8	19.7	18.1	148	166	2673
ALD1	7	6.68	2	186	10	-110	187	158	28.5	27.6	3.7	0.6	1.4	1.3	192	148	343
OPC1		2.84	9	566	19	953	0	0	135.0	117.5	99.2	74.2	18.1	16.9	243	241	2238
OPC2A		3.12	10	511	12	549	0	0	33.4	24.9	84.2	76.7	25.0	20.0	271	206	2177
CC1	45	7.44	10	178	13	-192	224	227	4.8	1.6	0.7	0.3	0.5	0.6	373	333	1496
VFP1	45	7.01	1	-108	15	-378	476	434	2.2	1.8	0.3	0.1	0.8	0.6	329	328	1222
OPC2		5.39	10	142	12	73	54	22	13.0	4.5	23.9	13.8	10.4	9.6	234	232	1408
SB1		5.39	10	242	12	54	10	9	4.0	3.1	10.0	8.1	10.4	10.1	255	177	1387
OPC3		6.42	9	176	13	24	16	16	1.9	1.1	5.1	4.1	7.8	7.5	229	138	1305
VFP2B	212	7.49	7	-127	12	-207	246	237	0.1	0.1	0.3	0.1	5.6	5.3	300	258	1095
SPWL2B		8.08	3	-18	14	-193	220	218	0.2	0.2	0.1	0.1	5.2	5.0	290	247	1060
HFLB	174	7.51	2	-7	12	-180	214	209	0.1	0.1	0.2	<0.1	5.3	4.4	298	256	1097

Average values; number of samples (n) varies; data available at www.datashed.org; flow in Lpm; pH in standard units not averaged from H-ion concentration; concentrations in mg/L; dissolved oxygen (DO), total (T) & dissolved (D) metals, oxidation-reduction potential (ORP) in mvolts; Temperature (T) in ^{0}C

“Porcupine Run” Before & After Passive System Installation

The impact of the passive system on the receiving stream, “Porcupine Run”, is quite dramatic as demonstrated in Table 6. After the installation of Phase 2, the majority of the mine water affecting sampling point 162-22 was being diverted into the passive system. As can be seen, “Porcupine Run” at this point is still influenced by mining, but the water quality is substantially improved. At point 162-24, over 300 meters (1000 feet) downstream of 162-22, the flow rate of “Porcupine Run” has more than doubled and the stream has become more degraded, reflecting the impact of additional AMD sources. Comparison of “Porcupine Run” at 162-24, which is about 15 meters (50 feet) upstream of the confluence with the passive system final effluent, with point 162-23, which is located approximately 30 meters (100 feet) downstream of the confluence, indicates that the effluent of the system improves “Porcupine Run” from a net acidic to net alkaline stream with decreased concentrations of iron and aluminum. At sample point 162-21 which is located about 300 meters (1000 feet) downstream of the passive system, the water has improved significantly. Other mine discharges located downstream of the passive system impact the stream, but at times the quality of “Porcupine Run” is net alkaline with relatively low concentrations of dissolved iron and aluminum and slightly elevated concentrations of manganese. Based upon available data, “Porcupine Run” at 162-21 remains, on average, slightly net acidic, but the overall improvement is still dramatic, as prior to installation of the passive system based on available monitoring spanning the previous 30 years (n=57), “Porcupine Run” characteristically had a pH of 3 or less with 500 mg/L acidity and 50 mg/L total iron as depicted in Table 6.

Table 6. Pre- and Post-Construction Water Quality Characteristics of “Porcupine Run”

Sample Site		**Flow**	**pH** Field	**Alk.** Field	**Acid.**	**Fe**		**Al**		**Mn**		**SO4**
						T	D	T	D	T	D	
162-22 *(below Ph.1)*	Pre-const.	163	3.77	15	597	73.0	31.8	45.9	20.0	16.2	6.4	1342
	Post-const.	83	6.17	41	4	3.3	1.9	5.0	3.0	12.3	12.0	1350
162-24 *(above Ph.2)*	Post-const.	182	5.26	6	36	11.8	11.3	2.3	1.4	8.1	7.9	804
162-23 *(below Ph.2)*	Post-const.	341	6.76	81	-37	7.1	5.7	1.2	0.7	7.1	6.8	920
162-21 *(below Ph.2)*	Pre-const.	261	3.03	0	498	50.6	15.2	26.5	17.6	21.1	13.4	1337
	Post-Ph. 1	242	4.34	2	64	4.9	4.5	5.4	4.6	17.6	17.0	1098
	Post-Ph.1&2	1208	6.00	22	12	3.8	1.9	3.5	2.2	12.7	11.7	829

Average values (n=24-26); flow in Lpm; pH not averaged from H-ion concentrations; concentrations in mg/L; specific conductivity (SC) in umhos/cm; T-total; D-dissolved; 162-24 and 162-23 post-construction values only (ref: www.datashed.org)

Preliminary Effectiveness of Iron Removal at Low pH

The Phase 1 portion of the system has exceeded all expectations especially in terms of low pH iron removal. On average about 233 mg/L (90%) of the iron is being removed at low pH simply by allowing the water to flow over a wide, flat-bottomed, rock-lined channel. Tables 7 and 8 provide a closer look at this phenomenon for select parameters on individual sampling dates. The lowest percent decreases in dissolved iron concentrations occurred on 12/21/09 and 1/21/10. Interestingly, these were also the coldest sampling events to date with much of the channel covered by a layer of ice. Despite the below freezing ambient temperature conditions and an ice cap over much of the channel, a 78% and 74% removal rate of dissolved iron on 12/21/09 and 1/21/10, respectively, still occurred. Also note that the calcium content of the drainage does increase, indicating some dissolution of the limestone (~70% $CaCO_3$) used for the riprap channel liner and/or influence from other drainage, which may at times contribute to the observed decreases in acidity.

Table 7. Selected Water Quality Data from “Snapshots” Demonstrating Iron Removal

		7/30/2008			3/24/2009			6/30/2009			9/28/2009			12/21/2009		
		OPCin Calc	**OPC2A**	**% chg.**	**OPCin Calc**	**OPC2A**	**% chg.**	**OPCin Calc**	**OPC2A**	**% chg.**	**OPCin Calc**	**OPC2A**	**% chg.**	**OPCin Calc**	**OPC2A**	**% chg.**
Flow		19.3	19.3	----	25.0	25.0	----	16.6	16.6	----	18.5	18.5	----	22.7	22.7	----
pH		2.72	3.1	----	2.83	3.21	----	2.64	3.04	----	2.79	3.1	----	2.74	3.15	----
ORP		521	542	----	468	458	----	467	487	----	446	557	----	441	481	----
DO		1	8	----	NM	NM	----	3	8	----	4	10	----	6	9	----
Acd.		1183	533	-55	1223	729	-40	1393	401	-71	899	332	-63	868	561	-35
Fe	T	248	19	-92	291	20	-93	304	15	-95	196	28	-86	195	56	-71
	D	240	13	-95	290	10	-97	288	15	-95	196	11	-94	193	43	-78
Al	T	240	86	-64	105	102	-3	106	109	+3	116	47	-59	79	69	-13
	D	186	73	61	105	103	-2	68	80	+18	96	47	-51	69	66	-4
Mn	T	19	28	+52	16	20	+28	18	18	+5	16	20	+20	17	45	+169
	D	18	21	+15	16	20	+20	17	18	+7	15	11	-30	13	32	+140
Ca	T	NM	NM	NM	NM	NM	----	NM	NM	----	107	172	+62	130	360	+176
SO4		2157	2359	+7	2615	2330	-11	2866	2627	-8	2253	1264	-44	2074	2052	-1

OPCin Calc - calculated value for OPC1 inlet from combined weighted average of ALD and Forebay data; flow in Lpm, pH in standard units; concentrations in mg/L; oxidation-reduction potential (ORP) mvolts; dissolved oxygen (DO); T-total; D-dissolved; NM-not measured; chg. -change; “---“ not calculated or not applicable

On January 21, 2010, a partial water quality “snapshot” and dye test was conducted as an initial attempt to better understand the processes occurring and possibly evaluate residence (retention) times for removal of iron at low pH. As the dye tended to cling to the channel substrate, a single dye test for the entire length of channel could not be completed. Sections of the channel that corresponded to sampling point locations were then independently reviewed. Based on the travel times through the individual sections, a cumulative time frame was developed. (Refer to Table 8 for selected data.) Approximately 74% of the total iron load was removed along an approximately 180-meter (600-foot) long section of the channel within about 90 minutes. Interestingly, the greatest decrease in loading for a particular segment in comparison to the loading at the start of that segment (~52%) occurred between OPC1 and OPC2B where the loading decreased from 10.2 kg (22.4 lbs) to 4.8 kg (10.7 lbs), in a distance of only 35 meters (115 feet). As this channel section had a comparatively steep slope, the retention time was only about 6 minutes. A significant corresponding increase in dissolved oxygen concentrations and pH also occurred in this time.

Table 8. 1/21/10 Water Quality and Dye Test Depicting Iron Removal at Low pH

Sample Site	**Flow**	**pH** Field	**ORP**	**DO**	**T**	**Alk** Field	**Acd.**	**Fe^{+2}**	**Fe**		**Al**		**Mn**		**Ca**	**% T. Fe load loss**	**Dist.**	**Time**
									T	D	T	D	T	D	T			
FB1	34	2.79	499	9	3	0	1368	157	318	295	104	100	19	15	264	NA		
ALD1	11	7.00	186	6	7	173	-126	0	<0.1	<0.1	0	0	0	0	99	NA		
OPCin (calc)	45	2.90	421	9	3	0	994	118	238	221	78	75	14	11	221	0	0	0
OPC1A	45	3.10	502	11	<1	0	940	90	218	195	99	94	12	12	220	9	42	15
OPC1	45	3.04	526	6	<1	0	872	32	155	144	91	66	13	12	243	29	99	60
OPC2B	45	3.32	515	11	<1	0	812	23	74	73	92	91	14	14	286	52	134	66
OPC2A	45	3.12	544	>13	<1	0	739	7	62	58	92	91	18	18	281	16	180	87

Flow (Lpm), pH in standard units; concentrations in mg/L; oxidation-reduction potential (ORP) (mvolts); dissolved oxygen (DO), T-total; D-dissolved; distance (Dist.) in meters; time in minutes

Literature Review and General Discussion of Iron Removal at Low pH

While the results are extremely encouraging, questions do remain. A review of just a small portion of the available literature tends to point toward the importance of iron-oxidizing bacteria; however, a variety of other biogeochemical factors may play a role as well. Some potential factors affecting low pH iron removal may include: iron concentration, retention or travel time, species of bacteria present, concentrations of bacteria, pH, ORP, dissolved oxygen, temperature, nutrients, presence of rough edges for bacteria and iron attachment sites, depth of water, channel slope, sunlight, presence of other dissolved ions, etc.

Thiobacillus ferrooxidans and other acidophilic chemolithotrophic bacteria have been identified as being able to increase the rate of oxidation of Fe^{+2} to Fe^{+3} at pH below 3.5 (Kleinmann, et al, 1981). A study completed by Okereke and Stevens in 1991 which investigated the role of temperature as well as bacterial cell, ferrous, and sodium concentrations on Fe^{+2} oxidation rates found that these factors accounted for about 68%, 20%, 1.5%, and <1%, respectively, of the total variation within the study (Okereke, et al, 1991). The same study found a doubling of the oxidation rate when both temperature increased between 10°C and 20°C and bacterial concentration increased between 0.25 and 0.50 mg/ml; however, the study also showed that independently the concentration of *T. ferrooxidans* was the single most important factor and that, as an independent factor, temperature had little effect, which correlates well with our observation of iron removal during the winter.

Burgos, Senko and Bruns (Burgos, et al, 2007) investigated factors influencing differences in low-pH iron removal occurring naturally at two sites with somewhat similar water quality. Not unlike our experiences and the study conducted by Okereke, they found that iron oxidation occurred regardless of time of year, but a slight decrease in the oxidation rate did occur during winter. By comparing the iron removal at the two sites, they also concluded that by maximizing the residence time and aeration of the mine water flowing over the iron sediments that an efficient and low-cost system could be implemented at these sites (Burgos, et al, 2007). In addition, there was evidence that the iron oxide sediments themselves may then act as a catalyst thus further promoting iron removal at low pH.

Conclusion

Two acidic abandoned mine discharges with high concentrations of iron and aluminum are being effectively treated with an innovative passive treatment system. In addition to a variety of treatment components, the passive system includes the use of Oxidation and Precipitation Channels (OPCs) to remove iron at low pH in order to reduce operation and maintenance concerns and extend the life of the system. Available literature indicates that the success of the OPC is most likely a result of iron-oxidizing bacteria performing at ideal conditions. Other design considerations included creating elk habitat, decreasing the potential for saturation with respect to gypsum, increasing alkalinity through anaerobic decomposition and sulfate reduction in existing net alkaline mine drainage sources to aid in treatment of the acidic drainage and reduce the amount of limestone needed. The final effluent of the system can be characterized as net alkaline with total iron and aluminum less than 1 mg/L and total manganese less than 6 mg/L. Improvements to the receiving stream have been substantial.

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