SUSTAINABLE PASSIVE TREATMENT OF MINE DRAINAGE: DEMONSTRATION OF MANGANESE RESOURCE RECOVERY(A Preliminary Case Study) [1]

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Abstract: Passive treatment system components containing limestone are an effective means to decrease Mn concentrations in coal mine drainage. As precipitates, sediment, vegetation, and other materials accumulate in the void spaces, permeability decreases and treatment effectiveness is reduced. Recently, the ability to recover manganese-bearing material for potential economic use while restoring treatment efficiency has been demonstrated at the De Sale Phase 2 passive treatment system, installed at an abandoned surface coal mine in western Pennsylvania. Efforts to date include pre- and post-recovery water monitoring; development of a unique "full-scale" recovery technique; preliminary physical, chemical, and mineralogical analysis; and identification of a potentially economically-viable use of the recovered material. The horizontal flow limestone bed was monitored 3, 24, 64, and 118 days after Mn recovery. Comparing the influent with the effluent indicated decreases in dissolved Mn concentrations from 64 to 30 mg/L, 55 to 10 mg/L, 46 to 9 mg/L, and 20 to 8 mg/L, respectively, essentially doubling treatment effectiveness. Over 40 cubic yards (30 cubic meters) of manganese-bearing material were recovered. Currently, the Mn material is being used by local ceramic artists as a glaze colorant and is being evaluated by other industries including brick manufacturing.

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Introduction

Mine drainage from abandoned sites is an international issue. In Pennsylvania, abandoned mine drainage is the largest non-point source of stream impairment. According to the 2006 Pennsylvania Integrated Water Quality Monitoring and Assessment Report, over 4,600 miles (7,400 km) of streams have been degraded. In many cases, entire watersheds have been completely decimated.

Passive systems typically use no electricity, require limited maintenance, and use environmentally friendly materials, such as limestone aggregate and spent mushroom compost in a series of constructed ponds, beds, ditches, and wetlands. As with any type of system, the goal is to provide economical, long-term, effective treatment. Passive components are selected based upon the often variable quality and flow rate of the mine drainage, preferred chemical and/or biological processes, and available construction space.

One of the many effective components available to designers of passive treatment systems is the Horizontal Flow Limestone Bed (HFLB). An HFLB is an open, unburied, bed of limestone aggregate, which is commonly installed as the final component in a passive treatment system. The HFLB serves two major purposes. First, the HFLB provides an alkalinity "boost" to the final effluent, which adds buffering capacity to the stream, which in many cases is much needed in order to lessen the impact of other acidic sources downstream. Second, the HFLB is effective in removing dissolved Mn.

Historically, removal of dissolved Mn from mine drainage has been problematic and thought to require chemical treatment in order to raise the pH above ≈ 9. With the development of passive technology, dissolved Mn has been observed to form solids at a much lower pH (6 to 7). The exact mechanism is not completely understood at this time, but biogeochemical factors such as low dissolved ferrous iron concentrations, high dissolved oxygen concentrations, available surface area, sufficient alkalinity, presence of certain microorganisms, and autocatalytic processes appear to play a significant role (Rose, 2003). The availability of certain nutrients, dissolved organic carbon, and other factors may also be important, depending upon the role and type of the microorganisms in the removal process (Dr. William Burgos, personal communication, 11/2007).

The HFLB, as well as many other effective passive components, accumulates metal precipitates, sediment, vegetative debris, etc. Over time, the accumulation of these materials can result in decreased treatment efficiency as the treatment media becomes plugged and permeability decreases.

Manual removal of the surface debris has been conducted and various methods have been used to restore the permeability of the treatment media, including flushing, backflushing, stirring, etc. While these methods can be effective for some passive components, for others the impact to the overall functionality and effectiveness has been minimal or short-lived. In some cases, the treatment media was actually removed/discarded and subsequently replaced even though the media still possessed significant treatment capabilities. Decreased functional life expectancy of the component increases long-term operation and maintenance costs and in some cases can lead to the perception that passive treatment is too costly, ineffective, and/or unreliable.

The authors have developed a method for the rehabilitation of treatment media that not only restores the efficacy and functionality of the component, but also facilitates the reuse of viable treatment media and the recovery and use of the accumulated material as a resource. Another aspect that makes this approach unique is that the recovery system is readily portable (even to remote locations) with a quick set-up time. While the following is a case study of the first attempt at rehabilitation of an HFLB and the simultaneous recovery of Mn, this process could potentially be used for other passive components and metals as well.

Project Location

The first full-scale attempt by the authors to rehabilitate an HFLB and simultaneously recover Mn was conducted at the De Sale Restoration Area Phase II Passive Treatment System located in western Pennsylvania about 50 miles (80 km) north of Pittsburgh in Venango Township, Butler County. More specifically, the site is about 2 miles (3 km) west of the town of Eau Claire along State Route 58 at latitude 41° 08’ 40” and longitude 79° 49’ 55” (BioMost, 2002). (See Fig. 1 or go to www.datashed.org.)

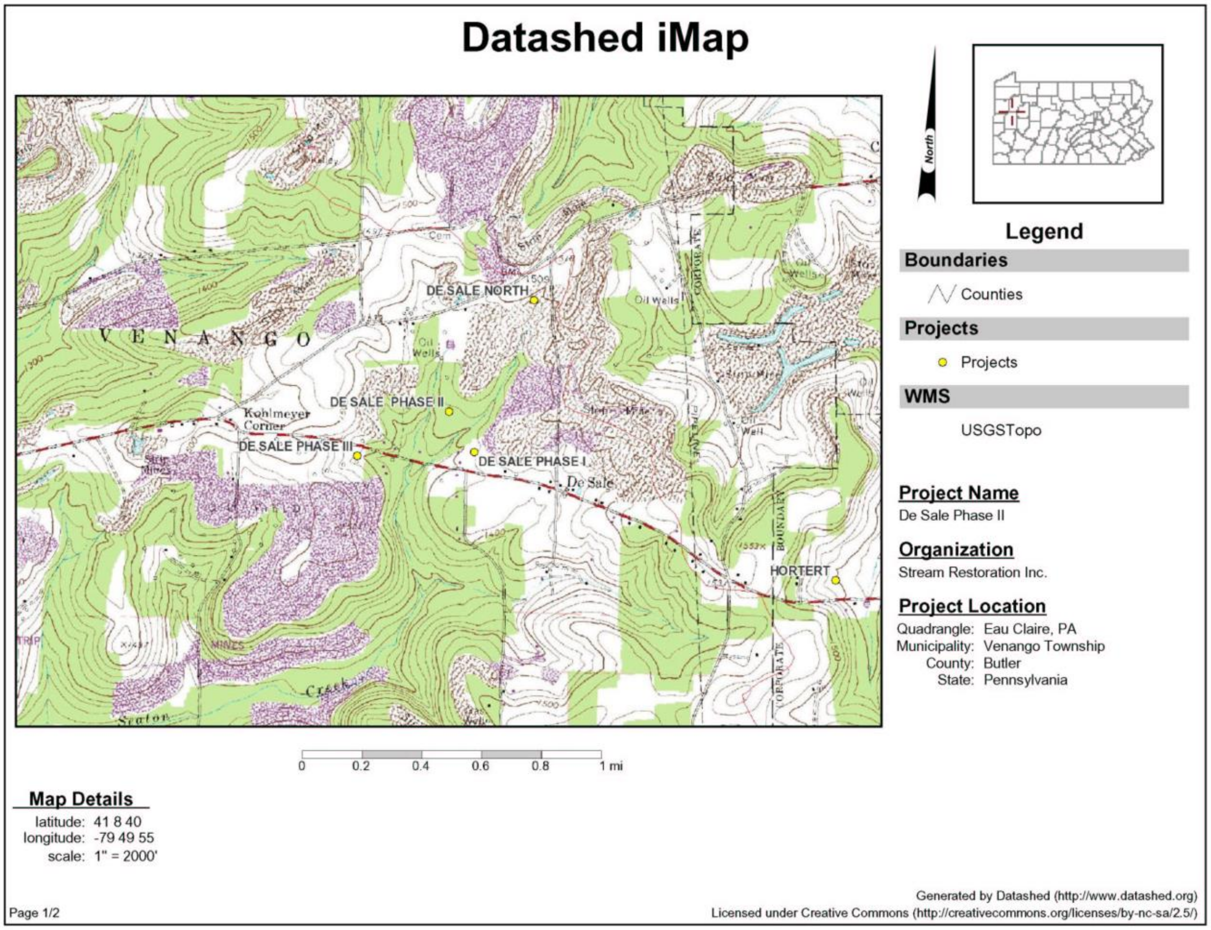

Figure 1. De Sale Phase 2 Location Map generated by www.datashed.org

Site History

Coal extraction activities conducted prior to the implementation of the federal Surface Mining Control and Reclamation Act of 1977, severely impacted Seaton Creek, one of two major tributaries within the headwaters of the Slippery Rock Creek Watershed (Ohio River Basin). The essentially "dead" Seaton Creek was identified as the most heavily impacted tributary in the watershed (PA DEP, 1998). In 2000, through the generosity of a landowner, a public-private partnership effort involving a watershed group, nonprofits, mining companies, environmental consulting firms, and government agencies, was formed to address the problem. In August 2000, the De Sale Phase II passive system was constructed to treat a headwaters tributary to Seaton Creek. The primary source of flow to the unnamed tributary was toe-of-spoil drainage and runoff from an abandoned surface mine (ca. 1960) on the Middle Kittanning coalbed (Kittanning Fm.; Allegheny Gp.) (BioMost, 2002).

Passive Treatment System Description

The passive system consists of seven components (See Fig. 2). A stream intake, installed upon approval by the US Army Corps of Engineers, captures the flow, except during excessive storm events, of the small-unnamed tributary. From the intake, the flow is directed through a long narrow forebay with the effluent split between two Vertical Flow Ponds, each containing about 2200 tons (1996 metric tons) of limestone (90% $CaCO_3$) aggregate (AASHTO #1: 4" x ¾") overlain by about ½ foot (15 cm) of spent mushroom compost. The effluent of the two Vertical Flow Ponds is then conveyed by adjustable risers to a settling pond before entering a 1½-acre (0.6 hectare) aerobic wetland. From the wetland, the effluent is conveyed to an HFLB, containing 2900 tons (2631 metric tons) of limestone with the same size consist and quality as used in the VFPs, prior to being returned to the unnamed tributary (BioMost, 2002).

Passive System Performance

The De Sale Phase II passive system has been successfully treating acidic, metal-laden, mine drainage with widely varying flow rates for nearly eight years. Table 1 depicts the general treatment and effectiveness of the system (Maximum design flow: 200 gpm (757 lpm). The actual measured flow rates have ranged from 10 to 445 gpm (38 to 1685 lpm).

Table 1. De Sale Phase II Passive System Influent and Effluent Values (range)

Point	**Flow** (gpm)	**F. pH** (s.u.)	**F. Alk** (mg/L)	**L. Alk** (mg/L)	**Acidity** (mg/L)	**T. Fe** (mg/L)	**D. Fe** (mg/L)	**T. Mn** (mg/L)	**D. Mn** (mg/L)	**T. Al** (mg/L)	**D. Al** (mg/L)
Raw		2.9-4.5		0	92-451	7-82	8-37	18-84	11-77	2-15	5-13
Effluent	10-445	5.8-7.7	22-219	6-250	-73-35	0-15	0-6	0-51	3-46	0-3	0-1

Number of sampling events and sampling dates vary for each point and for individual parameters; field (F) or lab (L) measurement; total (T) or dissolved (D) metals

Based upon available data, an estimate of loading reduction reveals that over the past seven and a half years approximately 60,000 to 80,000 lbs (22,000 to 30,000 kg) of Mn have been retained within the passive treatment system that would have otherwise entered Seaton Creek.

By 2003, the accumulation of Mn as well as other metals, sediment, vegetation, etc. resulted in the HFLB component having small pockets of standing water. During high flow periods, a portion of the influent water would flow across the top of the HFLB and over an emergency spillway instead of flowing through the stone, which reduced treatment effectiveness.

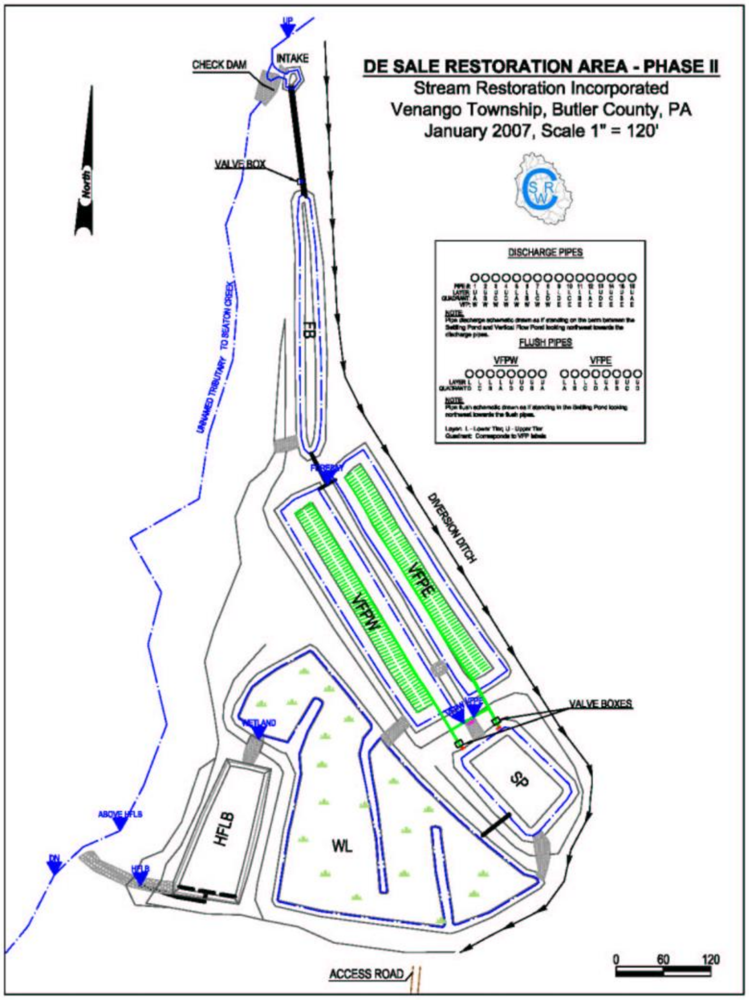

Figure 2. De Sale Phase 2 Site Schematic available at www.datashed.org

Initial Attempts to Rehabilitate the Horizontal Flow Limestone Bed

Prior to the effort in 2007, several previous attempts were made with varying success to rehabilitate the HFLB at De Sale Phase 2. In March 2004, the 10-inch (25.4 cm), perforated manifold installed along the width of the HFLB was backflushed at ~15 psi (103 kPa) using an air compressor. Backflushing was conducted to remove solids from the pipe and in the aggregate in the vicinity of the perforations. Manganese "chips" were observed in the flush water, indicating that at least a portion of the plugging was probably due to the precipitation of Mn within and near the pipe. Backflushing did lower the water level in the HFLB; however, the water level was still higher than the design elevation, indicating plugging within the bed. In April 2004, a small track loader was used to "stir" the upper portion (~2-3 feet) (0.6–0.9 m) of stone. In addition to vegetative growth, including what appeared to be algal (?) mats, Mn material was observed on the limestone aggregate and in the void spaces (See Fig. 3). The impact of the backflushing and stirring events was short lived. In October 2004, a trench was excavated at the beginning and the end of the HFLB, exposing the manifold collection pipe. In addition, the outlet piping was reconfigured to provide the ability to raise and lower the head as well as drain the HFLB. During this work, the pond was drained and the vegetative material and manganese-bearing precipitates on the surface of the bed were allowed to dry, "breaking up" some of the accumulated material. This effort resulted in improved flow through the bed with the water level remaining below the surface of the stone for one year. After that period, the water level again began to rise and typically a small portion was observed discharging through the emergency spillway. A new approach was required.

Figure 3. Manganese material filled void spaces and coated limestone aggregate prior to recovery

Rehabilitation and Resource Recovery Process

Shortly after the initial backflushing event during the period of 2004-2005, the authors were also examining the possibility of removing and recovering the Mn precipitates. During this investigation, samples of Mn solids were collected and analyzed indicating that the MnO could be considered an "ore" of Mn, containing about 50% Mn on an "as-received" basis and about 20% Loss On Ignition (LOI), which typically accounts for water, volatiles, and organic matter. Initial research indicated the Mn was suitable for use in ceramic glazes as well as other uses. A grant was received in 2006 through the Pennsylvania Department of Environmental Protection

Bureau of Abandoned Mine Reclamation (PA DEP BAMR) to further investigate and develop a method to economically recover and use the Mn material as a resource.

Through a literature and Internet search and bench-scale studies, a proposed method to simultaneously restore the efficacy and functionality of the HFLB and to recover the material was developed. This was accomplished through the use and combination of several existing products or conceptual ideas into a unique process that, to our knowledge, had not been previously attempted. One aspect that makes this system unique is the portability and quick set-up time of the recovery system (even in remote locations).

The first implementation of this process was conducted in August and September of 2007 at the De Sale Phase 2 passive treatment system. The influent flow was bypassed and the HFLB was drained. (During this seasonal low-flow period, the drainage was adequately treated by manipulating the flow through the other passive components.) Two wash pits were excavated within the HFLB, lined with impermeable material, and filled with water from the treatment wetland using a small pump. Using an excavator with a rotating screen attachment called a Flip Screen (Flip Screen Australia Pty Ltd., New South Wales), the bucket was filled with the limestone aggregate and the Mn-bearing material was removed by rotating the Flip Screen within the wash pit (See Fig. 4 and 5). Material passing the 3/8-inch (0.95 cm) screen settled within the wash pit while the limestone aggregate remained in the bucket. (Note that screens with different size openings are readily interchangeable.) The now clean and refurbished treatment media was then returned to the HFLB. The slurry was generally pumped into flexible intermediate bulk containers (FIBC) held in place with a frame structure for settling and dewatering. In some cases, the water in the wash pit was allowed to evaporate and was then excavated (See Fig. 6) and stockpiled on a pad for additional drying prior to placement in an FIBC. Thirty-two bulk containers, each containing approximately one ton of recovered material, were removed from the site. In addition, an estimated 25-50 tons (23-45 metric tons) of recovered material was left within the wash pits for future removal.

Preliminary Evaluation of Effectiveness of HFLB Rehabilitation

As the rehabilitation and recovery effort was completed in September 2007, only the preliminary short-term effectiveness of the process can be described. Water sampling of the HFLB influent and effluent was conducted 3, 24, 64, and 118 days after completing the recovery effort. Table 2 provides the post-rehabilitation results for selected parameters.

Figure 4. Excavator with FlipScreen attachment “washing” Mn covered limestone

Figure 5. Close up of FlipScreen during manganese recovery operation

Note that the influent to the HFLB is consistently an alkaline, circumneutral, net-acidic, Mn-bearing (20 to 65 mg/L) drainage with low dissolved concentrations of Fe and Al. On days 24, 64, and 118, the effluent is characterized as net alkaline with dissolved Mn concentrations <10 mg/L. Post-rehabilitation monitoring indicates that, on average, the Mn concentration is decreased by about 32 mg/L (70%) compared with the average of 12 mg/L (35%) removed prior to rehabilitation. Further, a comparison of the loading reductions indicates that in the spring of 2007 prior to rehabilitation, the HFLB was removing about 30% of the Mn loading while post-rehabilitation monitoring indicates a 75% loading reduction.

Figure 6. View of recovered manganese material excavated from wash pit

Prior to rehabilitation, the water level in the HFLB was at or near the surface across the entire length of the bed (See Fig. 7). The Mn removal rate was calculated as 0.008 pounds/day/ton of stone. The hydraulic gradient was significantly increased from the rehabilitation effort, which resulted in less limestone being utilized for treatment (See Fig. 7). Based on the gradient and other factors, a rough calculation indicates that only about 2/3 of the treatment media is currently being used. The Mn removal rate is currently 0.012 pounds/day/ton of stone. Review of pre- and post-rehabilitation conditions indicates that the efficacy of the HFLB has improved. Additional monitoring and evaluation is recommended to further document and verify the long-term improvement.

Recovered Material Analysis and Characterization

Samples from 4 of the 32 totes were collected for laboratory testing, including particle-size distribution, bulk chemical analysis, and x-ray diffraction. Not all of the results from these analyses were available at the time of writing this paper. Grab samples of the material directly from the HFLB were collected by hand in 2005. Laboratory analyses indicated that the material was about 50% Mn on an as-received basis with a loss-on-ignition of about 20%. X-ray diffraction conducted on the samples revealed that the Mn material was a mixture of todorokite and birnessite. Preliminary X-Ray Fluorescence (XRF) results of the material recovered in 2007 report major oxides about 25% MnO, 25% SiO_2, 10% Al_2O_3, 10% CaO, and 25% Loss-on-Ignition. Limestone and quartz were identified by visual examination using a hand-lens. The material fizzed aggressively with 10% HCl indicating the presence of limestone as well as with H_2O_2 indicating the presence of Mn oxides. The preliminary analyses suggest that the recovered

Mn has become diluted primarily with limestone and quartz by the recovery process. Future efforts will include attempts to improve the recovery process to minimize dilution of the Mn material and to examine beneficiation processes to remove impurities.

Table 2. Post-Rehabilitation Influent and Effluent Water Quality of De Sale 2 HFLB

	3 days		**24 days**		**64 days**		**118 days**	
Parameter	**In**	**Out**	**In**	**Out**	**In**	**Out**	**In**	**Out**
Flow	10	10	40	40	83	83	250	250
pH (field)	5.08	6.49	6.42	6.93	6.86	6.76	5.58	6.53
ORP	316	279	169	158	153	141	245	176
DO	7.27	5.08	7.57	1.33	9.35	2.28	10.63	8.43
Temp.	22.5	18.7	20.0	18.1	10.8	8.8	3.9	2.9
Alkalinity (field)	16	58	18	87	36	71	7	25
Alkalinity (lab)	2.47	42.25	12.90	82.74	30.78	66.57	3.24	26.45
Hot Acidity	117.11	4.66	81.59	-73.04	54.90	-52.15	39.20	-12.81
T. Fe	0.25	0.19	0.16	0.05	0.56	0.07	0.44	0.10
D. Fe	0.23	0.13	0.10	0.02	0.48	0.06	0.34	0.02
T. Mn	64.83	30.78	55.12	9.84	47.44	8.77	20.41	8.59
D. Mn	63.83	30.14	54.89	9.78	46.38	8.67	19.82	7.77
T. Al	3.43	0.24	0.48	0.26	0.38	0.23	2.19	0.25
D. Al	3.25	0.09	0.13	0.08	0.30	0.15	0.93	0.18
SO4	1279.8	1297.1	1308.3	1322.0	1131.7	1123.9	538.6	519.5

Flow in gallons per minute; pH in standard units; ORP in mV; Dissolved Oxygen in mg/L; Alkalinity and Acidity in mg/L as $CaCO_3$; Total (T) and Dissolved (D) Metals in mg/L; Sulfates in mg/L;

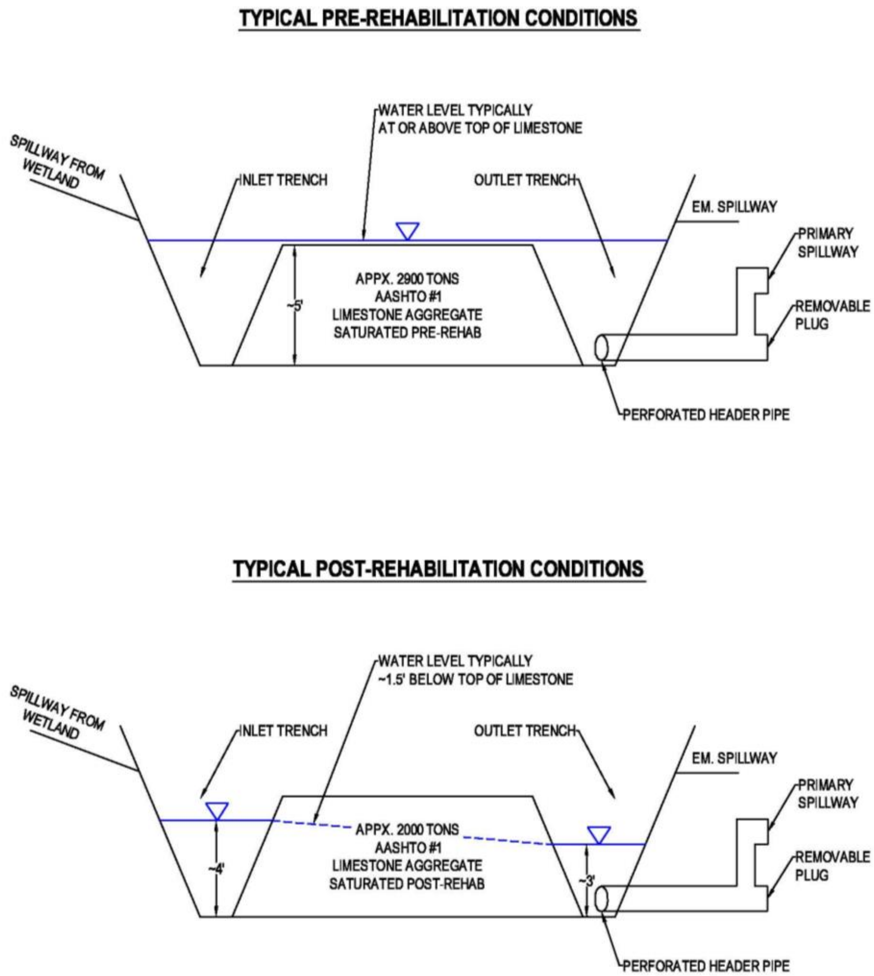

Figure 7. Typical Pre- and Post-Rehabilitation Conditions of the HFLB

Potential Uses

While Mn is used in a variety of products and processes including steel, batteries, chemicals, fertilizers, animal feeds, etc., current markets targeted include the use as colorants in bricks and cement and in ceramic glazes (BioMost, 2005). The recovered material is currently being utilized in ceramic glazes (See Fig. 8) and demand is growing. Over 300 hand-thrown pieces by local artisans have been sold or are on order. The colorant is also being sold by non-profits as a "green product" to the ceramics industry.

Conclusions and Recommendations

A method that effectively restored the efficacy of the De Sale Phase 2 Horizontal Flow Limestone Bed, reused the treatment media, and recovered Mn material for "recycling" has been demonstrated. Further investigations and marketing research, however, are needed to determine the commercial value of the product. In addition, continued and expanded monitoring of the HFLB is necessary to evaluate long-term treatment improvement. Research is needed to either improve the recovery process or develop efficient economical beneficiation process.

Figure 8: Examples of pottery with glazes using recovered Mn and Fe oxides formed at low pH

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