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TECHNICAL ARTICLE

Passive Removal of Mn from Mine Water Using Oxic Aggregate Beds: Results of Two Pilot Systems

Robert S. Hedin[1] · **Neil Wolfe**[1] · **Benjamin Hedin**[1]

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Abstract

In the U.S., the state of Pennsylvania has proposed lowering its Mn criterion from 1.0 to 0.3 mg/L. An investigation of the feasibility of meeting this standard with passive treatment was conducted. Existing data from 19 full-scale oxic limestone beds were compiled from literature reports to determine current Mn removal effectiveness and rates. The median system decreased Mn from 20 to 1.7 mg/L at a theoretical retention time of 37 h. Only two passive treatment systems produced effluents with < 0.3 mg/L Mn. In order to explore the capabilities of oxic limestone beds to remove Mn, two experimental oxic aggregate beds were installed at conventional AMD treatment plants and used to experimentally treat a portion of each plant's final effluent. The Hollywood unit was marginally effective, decreasing Mn on average from 0.584 to 0.281 mg/L with a theoretical retention time (TRT) of 3.7 h. The Brandy Camp unit was highly effective, decreasing Mn from 5.85 to 0.095 mg/L when operated at a TRT of 2.3 h. Effective removal of Mn by the Brandy Camp unit required 7 weeks of aggregate ripening. Average Mn removal rates for the Brandy Camp unit were 22.7 $g/d/m^2$, 15.7 g/d/mt, and 2.5 mg/L/hr of theoretical retention time. The half-time of Mn removal was 25 min. After one year of operation, hydraulic problems associated with the accumulation of iron solids on the surface of the aggregate forced termination of the Brandy Camp unit. The results indicate that the 0.3 mg/L effluent criterion can be achieved with oxic aggregate beds at very short retention times, as long as aggregate permeability is maintained.

Keywords Manganese removal · Pilot studies · Passive treatment

Introduction

Manganese (Mn) is a common component of mine waters that is included in most effluent permits because in excessive concentrations, it creates aesthetic, ecological, and human health problems (Grandjean et al. 2014; World Health Organization 1993). The instream Mn criterion generally ranges around the world between 0.3 and 1.0 mg/L (Strosnider et al. 2020). In the 1980's, the U.S. Environmental Protection Agency developed effluent limitation guidelines (ELGs) that placed restrictions on the amount of Mn that can be legally discharged in mining effluent at permitted sites. U.S. federal mining regulations effectively limit discharges of Mn at permitted coal mines to 2.0 mg/L as a 30 day average, 4.0 mg/L as a daily maximum and 5.0 mg/L as an instantaneous maximum (U.S. Code of Federal Regulations 1985). In Pennsylvania (USA), the instream criterion for Mn is 1.0 mg/L (25 Pa. Code § 93.7). Depending on the flow rate of the receiving stream relative to the flow rate of the mine discharge, the permitted effluent limits for Mn are driven by either federal ELGs or the instream criterion. A similar approach is used to establish permit limits at mine sites around the world.

In 2019, the Pennsylvania Department of Environmental Protection (PADEP) reevaluated its Mn standards and determined that Pennsylvania's current 1.0 mg/L Mn criterion does not adequately protect against neurological human health effects. Subsequently, the Pennsylvania Environmental Quality Board proposed adoption of a more protective human health criterion of 0.3 mg/L (PADEP 2020a, b). During the public comment period for the proposed regulatory change, objections were raised by industry representatives about the economic feasibility of meeting a 0.3 mg/L Mn standard (PADEP 2021). An analysis of the impact of the lower standard on the mining industry concluded that

✉ Robert S. Hedin
bhedin@hedinenv.com

[1] Hedin Environmental, Pittsburgh, PA, USA

passive treatment was not economically feasible, primarily due to system sizing challenges, and subsequently developed costs for the proposed 0.3 mg/L Mn standard using chemical treatment technologies (Burgos 2021). The estimated cost for the Pennsylvania coal industry to comply with the decreased Mn limits was $137–143 million in capital costs and $33–46 million in annual operations. Partially because of these cost concerns, the lower Mn standard has not yet been adopted in PA.

In 2022, PADEP initiated this investigation of the feasibility of meeting the decreased Mn effluent targets with existing passive technologies. The focus of the study was Mn removal by existing passive mine water treatment systems in Pennsylvania and experiments conducted at two chemical treatment facilities. At both experimental systems, a portion of the effluent from operating treatment plants was directed into open-top containers filled with limestone aggregate. Influent and effluent Mn chemistry was monitored under a variety of flow conditions. The goals of the project were to evaluate the ability of a passive aggregate approach to meet the proposed 0.3 mg/L Mn effluent criterion and to develop kinetic information that would improve estimates of the sizing of the systems. This paper provides a general review of the passive treatment of Mn in Pennsylvania and presents the results of the two pilot-scale systems.

Manganese Chemistry and Treatment Background

Soluble Mn occurs primarily as Mn(II) and the standard treatment is through its oxidation to Mn(III/IV) and, ultimately, precipitation as Mn(IV) solids. There are three oxidation mechanisms that result in removal of Mn: homogeneous abiotic oxidation, heterogeneous abiotic oxidation, and biotic oxidation (Morgan 2005; Neculita et al. 2019).

Homogeneous reactions occur in solution and involve chemical oxidants, atmospheric oxygen, or basic chemicals. Chemical oxidants such as potassium permanganate, hypochlorite, and ozone provide very rapid oxidation. Oxidation with atmospheric oxygen only occurs at environmentally relevant rates at pH values above 9.5 (Davies et al. 1989) and requires the addition of caustic chemicals. At pH values above 10, removal of Mn(II) as $Mn(OH)_2$ also occurs. Conventional chemical treatment operations typically remove Mn through oxidation with potassium permanganate or pH adjustment with sodium hydroxide. Both involve costly and hazardous chemicals and create large volumes of sludge.

Heterogeneous abiotic reactions involve the oxidation of Mn(II) by dissolved oxygen that has been adsorbed to a surface (Davies et al. 1989; Stumm et al. 1996). The heterogeneous mechanism occurs at environmentally relevant rates at circumneutral pH. Suitable sorption surfaces include Mn oxides (Stumm et al. 1996), ferric oxyhydroxides (Davies et al. 1989), and organic and inorganic substrates (Lennox 2016; Stewart 2022). Many drinking water plants treat Mn-contaminated groundwater in filters that contain sand that is coated with Mn oxides and remove Mn through heterogeneous oxidation (Breda et al. 2019; Bruins 2017; Bruins et al. 2014).

A third mechanism is the biotic oxidation of Mn(II). Fungi and heterotrophic bacteria have been shown to oxidize Mn (Santelli et al. 2010; Tebo et al. 2005). The chemolithoautotrophic oxidation of Mn(II), in a manner analogous to Fe(II) oxidation by bacteria, was recently demonstrated for a bacterial co-culture isolated from tap water (Yu et al. 2020). The Mn oxides produced through biotic activity could promote oxidation of Mn through the heterogeneous mechanism. The overlap of abiotic and biotic mechanisms makes distinguishing their respective significance difficult, especially in field settings.

Passive treatment of Mn occurs at pH 6–8 under oxidizing conditions. Passive technologies that require or promote reducing conditions, such as anoxic limestone drains, vertical flow ponds (e.g. SAPS, RAPS, anaerobic wetlands), and bioreactors do not remove Mn to any significant extent (Neculita et al. 2019). A variety of oxic passive treatment technologies have been installed that intentionally or unintentionally remove Mn. Aerobic wetlands remove Mn and have been a common treatment practice for 30 years (Hedin et al. 1994). Many passive treatment systems include oxic limestone beds as a final polishing step. While intended to assure a circumneutral pH effluent, the beds can remove Mn. The use of aggregate beds for targeted Mn removal was advanced in the late 1990s by Vail and Riley (1995, 1997) who developed and patented the Pyrolusite Process™, a Mn treatment technology that involved the inoculation of oxic aggregate beds with a proprietary microbial culture. Dozens of Pyrolusite Process™ systems were installed on coal mine sites in the eastern U.S. in the 1990s and early 2000s (Rose et al. 2003).

A common problem with oxic limestone beds is the buildup of metal solids that decrease bed permeability and aggregate reactivity. The problem has been addressed through oversizing of the beds and removal of solids through periodic cleaning or regular flushing. The drainable limestone bed concept involves the incorporation of a programable solar-powered gate valve that automatically drains the bed empty and removes a portion of the accumulated solids (Wolfe et al. 2010). Drainable limestone beds are intended for treatment of acidic waters containing Al and Fe; however, the removal of Mn also occurs (Hedin et al. 2022).

The type of aggregate used for Mn treatment has varied depending on mine water chemistry and availability. High calcite limestone (limestone with greater than 90% $CaCO_3$ content; hereafter referred to as limestone) is the standard choice for acidic waters where alkalinity generation and pH adjustment are needed. In systems receiving alkaline water, acid neutralization is not necessary and non-calcitic substrates such as dolomite and granite have been used as a substrate for Mn removal (Hedin et al. 2015; Johnson et al. 2005). The aggregate provides surfaces for the precipitation of Mn oxides and the development of microbial biofilms. In both processes, the amount of reactive aggregate is affected by surface area, which increases with decreasing particle size. Thus, the size of aggregate particles is considered an important variable in Mn removal systems (Means et al. 2005).

Methods

Experimental Sites

The experiments were conducted at two conventional AMD treatment plants operated by PADEP (Table 1). The Hollywood facility treats acidic underground coal mine discharges through aeration, lime, and polymer addition, and settling in a clarifier. The influent to the experimental system was obtained from the clarifier effluent. The Brandy Camp facility treats an acidic underground coal mine discharge with hydrogen peroxide, polymer, and lime slurry. Solids removal occurs in a series of ponds followed by a constructed wetland. The influent to the experimental system was obtained at the effluent of the constructed wetland.

At both sites, the experimental containers were open-top steel “roll-off” containers that were filled with limestone aggregate and plumbed to promote flow through the flooded aggregate (Table 1). The container used at the Hollywood site had a volume of 22 m^3 and contained 33 mt of aggregate obtained from a functional Mn treatment bed at a local passive mine water treatment system. This aggregate was already coated with Mn oxide and was selected to determine if delays in Mn removal that are common to passive systems (Hedin et al. 2015) could be avoided. The aggregate gradation was AASHTO #3 (ASSHTO 2013), which has an average particle diameter of 38 mm and a calculated surface area of 0.72 cm^2/g (Cravotta 2021). The container at the Brandy Camp site had a volume of 7.5 m^3 and contained 13 mt of aggregate obtained from a local limestone quarry. The aggregate gradation was AASHTO #8, which has an average particle diameter of 7 mm and a calculated surface of 4.44 cm^2/g (Cravotta 2021). In both systems, the influent water was introduced into the container on the surface via a perforated pipe and collected from the bottom of the tank in a perforated pipe. The water elevation in the aggregate was controlled by adjustments to the elevation of the effluent pipe outside of the tank.

Experimental Units Sampling and Analytical Methods

Water samples were collected from the influent and effluent of the experimental units. Field pH measurements were made using a calibrated electrode and field alkalinity was measured by titration to pH 4.5 using a digital titrator and 1.6N sulfuric acid. Dissolved oxygen (DO) was measured with a YSI ProSolo optical dissolved oxygen meter. Flow rates were measured by the timed-volume method. Water samples collected at both sites by the PADEP were analyzed by the Pennsylvania Bureau of Laboratories for a wide range of cations using EPA Method 200.7 (U.S. EPA 1994). The Mn detection limit was 0.010 mg/L. Samples reported at below this detection limit were entered as 0.010 mg/L Mn in data analysis spreadsheets. At the Brandy Camp site, a Teledyne ISCO© water sampler was used to collect samples from the effluent on frequencies that varied from twice/day

Table 1 Characteristics of the experimental units

	Hollywood	Brandy Camp
Location	41.240102, −78.538478	41.317050, −78.682750
Treatment Plant Process	Aeration, lime, polymer, clarifier	H_2O_2, lime, polymer, settling ponds, wetland
Water Source to Units	Clarifier effluent	Wetland effluent
Roll-off Empty Volume	24 m^3	7.5 m^3
Roll-off Dimensions[a]	6.6 m × 2.3 m × 1.6 m	3.6 m × 2.3 m × 1.0 m
Roll-off Surface Area	15.4 m^2	8.3 m^2
Aggregate Quantity	33 mt	13 mt
Aggregate Particle Size[b]	38 mm	7 mm
Aggregate Surface Area[b]	0.72 cm^2/g	4.44 cm^2/g
Aggregate Source	Mn treatment system	quarry

[a] Length X width X depth of aggregate

[b] Based on AASHTO classification and calculations from Cravotta (2021)

to every other day. Water samples were retrieved from the water sampler every 1–3 weeks and measured for Mn using a Hach DR 900 colorimeter and the Hach “high range” periodate oxidation method, with a reported detection range of 0.1–20.0 mg/L Mn, or the Hach “low range” PAN method, which has a reported detection range of 0.006–0.700 mg/L Mn. Analysis of blank samples (deionized water) returned 0.0 mg/L Mn for high range analyses and 0.000 mg/L Mn for low range analyses. Unless noted otherwise, all samples were unfiltered and the results represent total concentrations.

Table 2 shows a comparison of the Mn measurements by the PADEP and Hach methods for pairs of samples collected within 24 h of each other. Differences between the PADEP and Hach high range analyses were not significantly different. The DEP laboratory reported significantly lower concentrations of Mn than was obtained with the Hach low range method. 7 of the 21 analyses of Brandy Camp effluent samples were below the 0.010 mg/L of the laboratory. None of the 156 analyses made with the Hach low range method were below the 0.007 mg/L Mn detection limit. The reasons for the difference between the laboratory results is unknown. For data analysis purposes, on days when both analyses were available, the results were averaged.

Theoretical Retention Times

The theoretical retention time (TRT) of water within the passive treatment systems was calculated from the porosity of the aggregate divided by the flow rate, as shown below.

$$\text{TRT (hour)} = \text{aggregate}\left(\text{m}^3\right) \text{ X porosity (\%) X flooded stone (\%)} \; / \text{ flow rate}\left(\text{m}^3/\text{hr}\right) \tag{1}$$

where the aggregate beds were assumed to be 90% flooded with stone having a density of 1.6 mt/m^3 and a porosity of 40%. The porosity value, which is less than the 50% value used by Means et al. (2005), recognizes that the original porosity of the aggregate beds has lessened due to the accumulated of solids.

The porosity of the Brandy Camp unit, which contained fresh aggregate, was measured with sodium fluorescein tracer. A measured mass of tracer was added to the influent and the tracer was monitored at the effluent while measuring flow rate. The volume of the flooded aggregate was 6897 L. 50% of the recovered tracer was captured in 138 min which, at the influent flow rate of 22 L/min, was equivalent to 3082 L of flow (supplemental Fig. 1-S). The calculated porosity was 45%. This value was used in TRT calculations for the Brandy Camp and Hollywood units.

Mn Removal Calculations

Mn removal by the passive treatment systems and the units was evaluated by comparing influent and effluent concentrations and loads. Loads were calculated from the product of concentration and flow. Mn removal was related to measures of system size such as aggregate tonnage, aggregate surface area, and TRT. An approximation of the kinetics of Mn removal was calculated from the ratio of effluent and influent concentrations divided by TRT.

$$\text{k} = \ln\left(\text{Mn}^{\text{out}}/\text{Mn}^{\text{in}}\right)/\text{TRT} \tag{2}$$

The half time of the Mn removal was calculated from k.

$$\tfrac{1}{2}\text{ reaction} = 0.693/\text{k} \tag{3}$$

Kinetic calculations were limited to days when influent Mn, effluent Mn, and flow rate were all measured. Statistical evaluations were conducted using the Excel Data Analysis tools and the significance of evaluations was evaluated at the $P = 0.05$ level.

Results

Manganese Removal by Existing Passive Treatment Systems

The ability of oxic aggregate beds to remove Mn has been known for decades (Hedin et al 1994; Vail 1995, 1997). Table 3 provides system characteristics and Mn removal performance for 19 systems in Pennsylvania. Rose et al. (2003) reviewed Mn removal by nine Pyrolusite Process™ systems and developed a 1st order kinetic model for Mn removal. Luan et al. (2012) studied Mn removal in seven

Table 2 Comparison of reported Mn concentrations for samples measured by the PADEP laboratory and ones measured using Hach methods

	PADEP Laboratory	Hach Colorimeter	Paired t-test Result
Mn > 0.4 mg/L			
Method	EPA Method 200.7	Periodate oxidation	
Average	3.06	3.08	N = 8, P > 0.05
Mn < 0.4 mg/L			
Method	EPA Method 200.7	PAN	
Average	0.037 mg/L Mn	0.087 mg/L Mn	N = 11, P < 0.005

Table 3 Characteristics of 19 oxic aggregate beds and average Mn chemistry and flow

Site	Mn^{in}	Mn^{eff}	Al + Fe^{in}	Flow	Period	Bed Size		Stone size	TRT[a]	Mn Removal			Half Reaction	Source
	mg/L	mg/L	mg/L	L/min		mt	m^2	mm	h	mg/L/h	g/d/mt	g/d/m^2	h	
K&J	27.8	0.4	< 1	5.7	1991–98	112	58	25	82	0.33	2.0	3.9	13	(1)
Swisstock 1	16.4	4.4	6	110	1994–98	255	133	25	10	1.20	7.4	14.3	5	(1)
Swisstock 2	8.5	5.6	8	76	1995–98	62	32	38	3	0.97	5.1	9.8	5	(1)
PBS	28.1	1.1	5	25	1998–02	44	23	18	7	3.86	22.1	42.4	1	(1)
Laurel run	116	0.1	13	60	1997–02	1358	707	40	94	1.23	7.4	14.2	9	(1)
Stroud	8	1.2	6	46	1998–01	404	210	60	37	0.18	1.1	2.1	14	(1)
Glenwhite	5.7	0.4	29	255	1999–02	5500	2864	35	90	0.06	0.3	0.7	23	(1)
MB 1	20	6.7	19	140	2001–02	1282	668	60	38	0.35	2.1	4.0	24	(1)
MB 2	20	6.0	19	140	2001–02	1282	668	60	38	0.37	2.2	4.2	22	(1)
Ace	34.7	8.6	< 1	103	2009–10	510	266	na	21	1.24	7.6	14.6	10	(2)
Glady Fork	9.4	1.7	< 1	3252	2009	3706	1,930	na	5	1.54	9.7	18.7	2	(2)
De Sale 3	55.5	30.9	< 1	44	2009–10	259	135	na	25	0.98	6.0	11.6	30	(2)
De Sale 2	31.2	17.1	< 1	366	2009–10	2376	1,237	na	27	0.52	3.1	6.0	31	(2)
Fairview	150	70	8	38	2005–10	720	375	na	79	1.01	6.1	11.7	72	(2)
Derry Ridge	19.4	1.3	< 1	51	2009–10	1280	667	na	104	0.17	1.0	2.0	27	(2)
PBS	18.4	0.3	3	38	2006–10	784	408	na	86	0.21	1.3	2.4	14	(2)
West Box	11.9	2.8	28	4	2008–20	27	14	19	28	0.33	1.9	3.7	13	(3)
Scootac	23.5	1.6	10	160	2010–20	900	469	19	23	0.95	5.6	10.8	6	(3)
Greene	30.8	1.1	6	370	2015–22	5500	2,864	19	62	0.48	2.9	5.5	13	(3)
Median	20	1.7	8	76		784	408	30	37	0.52	3.1	6.0	13	
Average	33	8.5	12	278		1387	722	35	45	0.84	5.0	9.6	18	

[a] Theoretical retention time: see methods for calculation; "na" not available. Data sources: (1) Rose et al. (2003); (2) Luan et al. (2012); (3) system data from Hedin et al. (2022); stone size from Cravotta (2021)

oxic aggregate beds and conducted experiments that distinguished biotic and abiotic Mn removal processes. Hedin et al. (2022) reviewed Mn removal by three drainable limestone bed systems with a focus on sustainability and extent of Mn removal. All of the systems removed Mn, eight removed more than 20 mg/L Mn, and ten discharged less than 2 mg/L, which is equivalent to the 30 day average federal ELG. Only two of the systems discharged an effluent with an average concentration of 0.3 mg/L Mn or less. The systems received variable influent chemistries. For 13 of the systems, treatment of acidity, Al, and Fe was their primary purpose. The systems all contained limestone aggregate, but the gradation ranged between 18 and 60 mm. The size of the beds varied from 27 to 5500 mt. The mine water flow rates ranged between 4 and 3252 Lpm. The average theoretical retention times, calculated from the tonnage and flow, ranged between 3 and 104 h. The variable characteristics of the existing systems complicates specific determinations about Mn removal rates and processes. The experimental units were constructed to observe Mn removal in aggregate systems where chemical and hydrologic factors were less variable.

Influent Chemistry of the Experimental Units

Table 4 shows the average influent and effluent chemistries of the experimental units during the study. Both influents were alkaline with neutral pH. The influent at the Hollywood site contained 0.2–1.3 mg/L Mn. The influent at the Brandy Camp site contained 4.6–7.1 mg/L Mn. Both inflows also contained 1–2 mg/L Fe. Three rounds of sampling were conducted that included filtered (0.45 µm) and unfiltered samples. The analyses determined that at both sites, the influent Fe was predominantly particulate while the Mn and all other major elements were predominantly dissolved (data not shown). The influents of both sites contained DO in excess of the amount needed to oxidize Mn (0.3 mg/L DO per 1.0 mg/L Mn^{2+}).

Operation of the Hollywood Experimental Unit

Figure 1 shows sampling results for the Hollywood unit. The unit was constructed with aggregate obtained from an existing functional Mn treatment bed in an effort to avoid

Table 4 Influent and effluent chemistry of two experimental systems

Period	Units	Hollywood		Brandy Camp[a]	
		Nov'21 – Jun '22		Jul'22 – Jul '23	
		Influent	Effluent	Influent	Effluent
Samples	Number	32	32	21	21
pH	s.u	7.2	7.1	7.1	7.3
Alk	mg/L $CaCO_3$	39	38	131	143
Acid	mg/L $CaCO_3$	-21	-22	-105	-119
Fe^T	mg/L	1.4	0.6	1.7	< 0.1
Fe^{2+}	mg/L	0.3	< 0.1	< 0.1	< 0.1
Mn	mg/L	0.6	0.3	5.4	0.8
Al	mg/L	0.7	< 0.4	< 0.3	< 0.3
SO_4	mg/L	420	412	696	660
Ca	mg/L	143	139	219	232
Mg	mg/L	20	20	66	66
K	mg/L	3	3	5	5
Na	mg/L	7	7	17	17
Cl	mg/L	1	1	5	5
Zn	µg/L	18	10	40	9
Ba	µg/L	11	7	12	10
Ni	µg/L	37	21	60	20
Cations	meq/L	9.3	9.1	17.4	18.0
Anions	meq/L	9.6	9.4	17.3	17.5
TSS	mg/L	< 20	< 20	< 20	< 20
DO	mg/L	10.9[b]	–	9.7[c]	5.8[c]

All analyses by the PADEP laboratory

[a] Includes samples collected during Brandy Camp start up period

[b] Measured by Hedin Environmental Nov 4, 2021

[c] Measured by Hedin Environmental July 9, 2023

the treatment delay commonly observed for Mn removal beds using fresh aggregate (Hedin et al. 2022). The system received alkaline water with low concentrations of contaminants (Table 4). The average influent Mn concentration, 0.584 mg/L, was less than anticipated when the experiment was planned. The system decreased Mn on every sampling day (n = 40). Mn removal was not delayed during the startup period and the greatest decrease in Mn concentration occurred during the first month of operation. After the first month, Mn removal averaged 0.281 mg/L. During the subsequent nine month period, effluent Mn concentrations less than 0.3 mg/L only occurred when the influent water contained less than 0.6 mg/L. In August 2022, the influent flow rate was reduced and TRT increased from 2.5 to 5.0 h. Doubling the TRT only decreased effluent Mn by an additional 0.06 mg/L. None of the 32 effluent samples measured by the PADEP laboratory reported Mn below the laboratory's 0.010 mg/L detection limit.

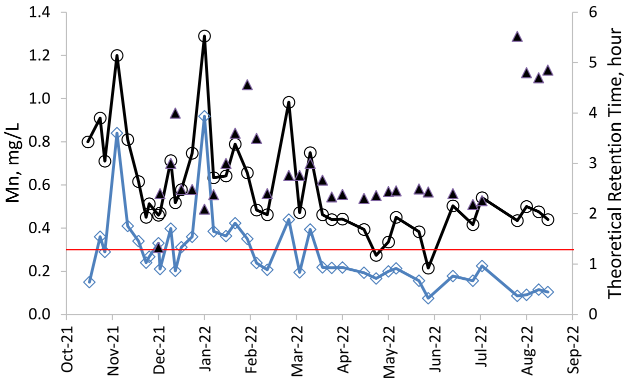

Fig. 1 Hollywood Unit: Theoretical Retention Time (▲), Influent Mn Concentration (—○—) and Effluent Mn Concentration (—◇—). The Red Horizontal Line is the Proposed 0.3 mg/L Mn Limit

Operation of the Brandy Camp Experimental Unit

Figure 2 and Table 4 provide sampling results for the Brandy Camp unit. The system was constructed with fresh aggregate. It was expected that Mn removal would be delayed due to a "ripening" process (Bruins et al. 2015). Mn removal was not observed in the first 2 weeks. Effluent Mn concentrations decreased to less than 2 mg/L after 4 weeks and to less than 0.3 mg/L after 7 weeks. The flow rates during the start-up period were 17–23 Lpm and the TRT averaged 2.4 h.

Following the startup period, the unit was operated between August 20 and November 7 at flow rates of 15–28 Lpm with an average TRT of 2.1 h. During this period, the effluent averaged 0.109 mg/L Mn. Of the 68 effluent measurements, only three exceeded 0.3 mg/L Mn and four measurements were below the 0.010 mg/L detection limit of the PADEP laboratory.

In November 2022, flow rates were increased to 50 Lpm and TRT decreased to 1 h to assess the Mn removal capabilities of the unit with higher loads. Unfortunately, under these conditions, the influent water passed across the surface of much of the aggregate, resulting in short-circuiting conditions. The hydraulic limitations were attributed to two problems: the mine water contained 1.5 mg/L of particulate Fe, which accumulated on top of the aggregate and lessened the permeability of the surface stone, and undersized piping. The system was designed with an expectation that the maximum flow rate treated would be 10 Lpm. The consequence of undersized plumbing and decreased aggregate permeability was the development of flow paths across the top of the aggregate instead of through it. This hydraulic problem invalidated the results obtained during high flow testing.

In December, the flow rates were decreased to 20–28 Lpm with an average TRT of 2.0 h. The effluent averaged 0.248 mg/L Mn (15 measurements). On December 23, 2022, local air temperatures fell to −25 °C and stayed below −10 °C for a week. During this period, the influent piping to the system froze and operations ceased. The bed was drained and not operated during the first two weeks of January 2023. On January 12, the influent plumbing was repaired and the flow through the unit was reestablished. While partial removal of Mn occurred immediately, consistent removal of Mn to less than 0.3 mg/L took two weeks (Fig. 2).

On February 2, 2023, the bed was disconnected and drained to avoid further cold weather disruptions. The unit remained off-line until March 20, 2023, when it was reflooded and restarted. Following the restart, removal of Mn to less than 0.3 mg/L was delayed for two weeks (Fig. 2).

In mid-April 2023, the Brandy Camp unit developed permeability problems that resulted in the backup of water within the roll-off container and partial overflows at flow rates that had previously been treated without hydraulic problems. The problems were due to the accumulation of Fe solids in the top 15 cm of the aggregate, which lessened permeability and limited flow to the underlying aggregate. When the surface aggregate was stirred or raked, water flowed down through the stone and overflows ceased. However, the iron solids were not removed and permeability issues quickly returned. During this period, the treatment performance of the bed (Mn removal and TRT) was evaluated from the flow rate and chemistry of the discharge from the effluent pipe. The overflow was ignored. On July 9, 2023, the permeability problem had increased to a point where 50% of the inflow was overflowing the unit and the experiment was discontinued. During the period between March 30 and July 9, when the unit was operated with moderate overflows, the final discharge had an average Mn concentration of 0.078 mg/L. None of the effluent samples exceeded 0.3 mg/L and seven were below the 0.010 detection limit of the PADEP laboratory. The average TRT during this period, calculated from the effluent flow rate (average 23.6 Lpm), was 2.7 h.

A common goal of passive treatment research is the identification of contaminant removal limits. The removal limits are determined by exposing a treatment unit to a range of influent loadings and identifying the conditions under which incomplete contaminant removal occurs. This type of experimentation was planned for the Brandy Camp system. However, the unexpectedly high Mn removal capability of the system combined with the hydraulic limits prevented operation of the system in an overloaded condition. Figure 3 is a plot of influent Mn loading against Mn removal. Overloading of the system never occurred and its maximum Mn removal capacity was not determined.

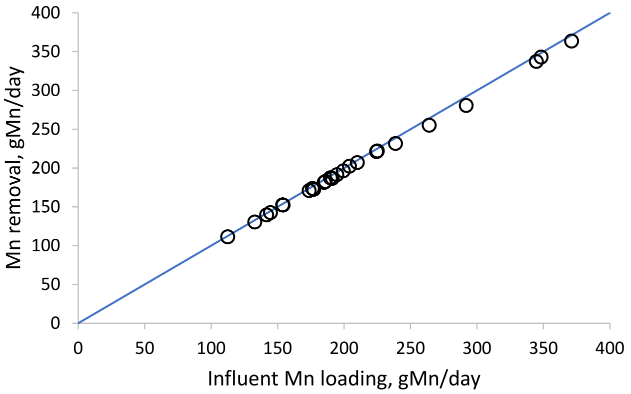

Fig. 3 Plot of Mn Removal, g/day, Against Influent Mn Loading, g/day for the Brandy Camp Unit. The Diagonal Line is 1:1 Correspondence

Discussion

Mn Removal Start-up Period

Delayed Mn removal is a common aspect of the start-up of oxic aggregate beds in drinking water and mine water treatment applications. Rapid sand filters, which are commonly used to treat groundwater containing 0.1–1.0 mg/L Mn, require weeks to months of operation to develop adequate Mn removal capabilities (Bruins et al. 2015). The delay,

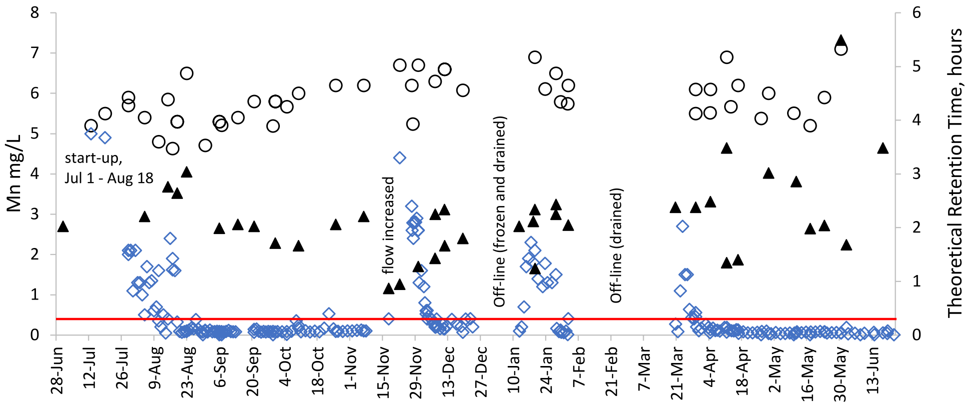

Fig. 2 Brandy Cam Unit: Theoretical Retention Time (▲), Influent Mn Concentration (○) and Effluent Mn Concentration (◇). The Red Horizontal Line is the Proposed 0.3 mg/L Mn Limit

which is referred to as "ripening", is due to the slow development of reactive Mn oxide coating on the sand. This delay can be lessened by mixing pre-ripened sand with unripened sand (Bruins 2017).

The Brandy Camp unit was installed and operated with a goal of documenting the start-up of a limestone bed treating Mn-contaminated mine water. The bed was constructed with fresh, un-ripened aggregate and treated water with 5–6 mg/L Mn with 2–3 h of TRT. The system required 4 weeks to consistently decrease Mn to < 2 mg/L and an additional three weeks to consistently decrease Mn to < 0.3 mg/L. This 4–7 weeks start-up ripening period is similar to ones observed for full-scale passive systems where Mn is treated with oxic aggregate beds (Hedin et al. 2015, 2022). During the experimental period, the Brandy Camp unit was shut down, drained, and then restarted twice. Mn removal was delayed for 2–3 weeks following each restart event.

The Hollywood system was constructed with aggregate from an existing functional passive system in order to test whether the initial ripening could be shortened. The unit immediately decreased Mn from 0.8 to 0.3 mg/L. The best performance of the unit, in terms of Mn removal, was observed during the first month of operation. In cases where a start-up period of two months cannot be accommodated, the treatment delay may be eliminated through the use of previously ripened aggregate.

Mn Removal

A primary goal of the project was to determine the feasibility of meeting Pennsylvania's proposed 0.3 mg/L Mn effluent limit using a passive aggregate approach. Data obtained from existing passive treatment systems shows that sustainable Mn removal is feasible, even in systems where the primary concern is removal of acidity, Fe, and Al (Table 3). Ten of the nineteen systems surveyed produced effluents that met (on average) the typical 2.0 mg/L Mn limit for U.S. mine sites. Only two of the systems produced average effluents of 0.3 mg/L or less. While meeting the lower Mn criterion appears feasible, achieving it on a regular basis will require modifications of passive treatment design or operations procedures.

The capability of the oxic limestone bed technology to meet the proposed 0.3 mg/L effluent limit was best demonstrated at the Brandy Camp system, which received an influent of circumneutral water containing 5–6 mg/L Mn. The system was operated without interruption for two months in fall 2022 and three months in spring/summer 2023. During these 180 days of operation, the average effluent concentration was 0.095 mg/L of Mn (Table 5). Only three samples contained > 0.3 mg/L Mn and 11 samples were below the PADEP laboratory's detection limits of 0.01 mg/L Mn. The results indicate that short-term compliance with the 0.3 mg/L standard is achievable with a passive aggregate approach as long as the hydraulic integrity of the system is maintained.

A secondary goal of the project was to determine if Mn removal to the proposed 0.3 mg/L effluent limit might be achieved with retention times shorter than the 24–48 h assumed in treatment system design software (Cravotta 2021). Both the Hollywood and Brandy Camp units were operated with TRTs of less than five hours. The Brandy Camp system consistently produced an effluent with less than 0.3 mg/L Mn at TRTs of 2–3 h.

The Brandy Camp site was selected in part because the presence of a conventional treatment system upstream of the unit assured that the influent water would be alkaline with low concentrations of Fe and Al. It was thought that the pre-treatment would eliminate issues associated with the accumulation of metals and solids other than Mn oxides. This assumption proved incorrect. The Brandy Camp influent contained 1.5–2.0 mg/L of suspended iron solids that

Table 5 Average Mn removal measurements for the passive treatment systems and the experimental units.

Parameter	Units	PTSs (N = 40)	Hollywood (N = 40)	Brandy Camp all Data	Brandy Camp Sustained[a]
Flow Rate	Lpm	278	58.2 (40)	24.7 (41)	24.5 (23)
Mn^{in}	mg/L	33	0.584 (40)	5.75 (57)	5.85 (35)
Mn^{eff}	mg/L	8	0.281 (40)	0.534 (234)	0.095 (144)
TRT	h	45	3.7 (40)	2.4 (41)	2.3 (23)
k	h^{-1}	−0.093	−0.236 (40)		−1.785 (23)
½ time	h	18	3.3 (40)		0.4 (23)
Mn Removal	mg/L/h	0.52	0.09 (40)		2.53 (23)
Mn Removal	g/d/mt	3.1	0.8 (40)		15.7 (23)
Mn Removal	$g/d/m^2$	6.0	1.6 (40		22.7 (23)

Samples sizes are in parentheses

[a] Periods not affected by start-up delays or hydraulic issues (Aug 20–Nov 7, 2022; Jan 28–Feb 2, 2023; Apr 4–July 7, 2023)

were filtered from the water by the aggregate bed. This accumulation of solids on the surface of the aggregate eventually decreased the hydraulic conductivity enough to affect the treatment performance of the unit. The Hollywood unit received a similar loading of particulate Fe but did not exhibit hydraulic problems. The Hollywood unit contained a larger aggregate than the Brandy Camp unit (Table 1) and may have had more capacity for solids accumulation. The sustained removal of Mn in aggregate beds at short TRT will require attention to the presence of solids that could adversely affect hydraulic conductivity.

Rates of Mn Removal

Contaminant removal in passive systems is often evaluated from a loading perspective where masses of contaminant removal are related to measures of system size such as surface area, volume, aggregate tonnage, or retention time (Hedin et al. 1994). This zero-order approach has proven useful for the design of passive systems for Fe removal (Hedin 2008). Table 3 includes TRT and Mn removal calculations for the 19 passive systems and Table 5 compares the summary values of the passive systems and the experimental units. The treatment systems had a median TRT of 37 h and removed 18 mg/L of Mn. This performance is consistent with the sizing default of 48 h contained in AMDTreat (Cravotta et al. 2015) and the 24–48 h TRT used to evaluate the feasibility of meeting a 0.3 mg/L Mn standard with an oxic aggregate approach (Burgos 2021). The Hollywood system is difficult to compare to the PTS because its Mn influent concentrations and loadings are very low and mass-based Mn removal rates are not appropriate. The Brandy Camp unit is a reasonable comparison as it received water with Mn concentrations that exceeded the existing (2.0 mg/L Mn) and proposed (0.3 mg/L Mn) effluent standards. Based on the various measures of the Mn removal made on bed tonnage (g/d/mt), bed surface area (g/d/m^2), and TRT (mg/L/h), the Brandy Camp system removed Mn 4–5 times faster than the median passive treatment system (Table 5). The average half-time of Mn removal by the PTS was 18 h. The average half-time for Mn removal by the Brandy Camp unit was 0.4 h.

Several explanations could explain the large differences in Mn removal between the passive treatment systems and the Brandy Camp unit. Most of the passive treatment system influents contained acidity, Fe, and Al in addition to Mn. A substantial portion of the aggregate bed would be involved in the removal of these other contaminants, not just Mn. In general, Mn removal is minimal when dissolved iron is present. Also, the accumulation of Fe and Al solids in aggregate beds decreases porosity and retention time. The TRT values in Table 1 certainly err high because they do not account for the loss of porosity to solids accumulation over years of operation. Additionally, Mn oxidation consumes oxygen, which can become limiting in beds that receive more than 20 mg/L Mn. The Brandy Camp system was not oxygen limited (Table 4) but many of the passive treatment systems have high concentrations of Mn that potentially resulted in portions of the bed becoming anoxic. The aggregate used in the Brandy Camp system was much smaller than the aggregate used in the passive treatment systems. Smaller aggregate provides greater surface area per mt and greater potential for heterogeneous and biological Mn removal. Investigations of aggregate beds that remove Mn commonly find that the active Mn-removing zone, indicated by birnessite-coated aggregate (Tan et al. 2010), is confined to a narrow band near the surface of the bed (Means et al. 2005; Hedin et al 2015). This suggests that the Mn removal reactions occur in a small portion of the beds and that many aggregate beds have unused Mn-removal capacity. Lastly, passive systems are designed for long-term performance with minimal operational requirements. This approach results in beds being intentionally oversized. It is likely that the rapid Mn-removal processes that occurred in the Brandy Camp system are also occurring in the full-scale passive systems, but the efficiency is masked by interference from other contaminants, inefficient hydraulics, dissolved oxygen limitations, and intentional oversizing to provide long-term treatment.

Future Research

The rapid removal of Mn by the Brandy Camp unit suggests that improved treatment by passive aggregate beds is possible. Additional research will enable this transition. The limit of Mn removal by the Brandy Camp unit was not determined because of difficulties encountered operating the system with high loadings. The Mn removal process in the Brandy Camp system was not identified. If the removal is biological, the nature of the biological agents (heterotrophic or chemolithoautotrophic) needs to be determined so that beds can be designed to optimize their activity. The importance of aggregate size also deserves attention. The Brandy Camp unit contained smaller aggregate than is conventionally used in passive systems. The larger surface area of the smaller aggregate likely contributed to the fast Mn removal. However, the smaller stone filtered solids and developed permeability problems. The balance between optimizing a bed's Mn removal capability and minimizing operational difficulties needs to be explored. The current research has shown that it is possible to meet the proposed 0.3 mg/L Mn effluent criterion with a passive aggregate approach and that the sizing of these treatment units can be an order magnitude smaller than is currently considered necessary. Operators of active treatment that would consider the technology will need to develop practices that assure removal of Fe solids ahead of the aggregate-based Mn removal beds.

Summary and Conclusions

Pennsylvania's Department of Environmental Protection has proposed lowering the State's Mn criterion from 1.0 to 0.3 mg/L. The ability of passive treatment with oxic beds of aggregate to meet the proposed criterion was investigated. Mn removal by 19 existing oxic aggregate beds was reviewed. Ten of the systems decreased Mn to less than 2.0 mg/L but only two had average effluents < 0.3 mg/L. Pilot scale oxic aggregate beds were installed to experimentally treat flows from chemical mine water treatment plants. The Brandy Camp unit received an influent with 5–6 mg/L Mn and was able to sustainably discharge effluent with less than 0.1 mg/L Mn. Mn removal rates, calculated from concentration and loadings, were 4–5 times greater at Brandy Camp than the passive treatment systems. Kinetic calculations determined that the half time for Mn removal at passive systems averaged 18 h while at Brandy Camp it averaged 25 min. However, the Brandy Camp unit eventually developed hydraulic problems due to the input and accumulation of iron solids. The results indicate that passive treatment can achieve the proposed 0.3 mg/L effluent criterion with oxic aggregate beds that are much smaller than ones currently being utilized. However, to achieve sustainable treatment, the influent must be free of suspended solids that would over time degrade the permeability of the aggregate.

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Data availability Data collected during the operation of the two experimental systems is available from the primary author.

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