

## Passive treatment of Mn: Results from an experimental pilot system

Benjamin Hedin, Neil Wolfe, Robert Hedin

Hedin Environmental, 195 Castle Shannon Blvd, Pittsburgh, PA, 15228, USA, ben.hedin@hedinenv.com

## **Extended Abstract**

Manganese (Mn) is a common water contaminant at coal and metal mine sites. Its treatment by conventional methods involves strong oxidants or caustic chemicals that are hazardous, expensive, and produce copious amounts of sludge. Mn can be treated passively in oxic aggregate beds by biological and/or physiochemical processes (Luan et al. 2012; Means and Rose 2005; Santelli et al. 2010; Santelli et al. 2011; Tan et al. 2010).

Pennsylvania's Department of Environmental Protection (PADEP) recently proposed to lower the current in-stream Mn criterion from 1.0 mg/L Mn to a human health-based criterion of 0.3 mg/L Mn (PA DEP 2020a; PA DEP 2020b). Public objections to the proposed changes included the high costs of meeting the standard with conventional chemical treatment (Burgos 2021). Passive treatment was not considered a practical option for high flows because of its large land requirements and uncertain ability to lower Mn to less than 0.3 mg/L.

In response to these concerns, a project was conducted that investigated 1) Mn removal by nineteen existing, full-scale passive treatment systems, and 2) two experimental, pilot scale oxic aggregate beds. While all full-scale passive systems removed Mn, only one system removed Mn below 0.3 mg/L Mn.

The two experimental, pilot scale units were located at two large conventional mine water treatment systems in Pennsylvania (Hollywood and Brandy Camp) and received Mn-contained effluent from the systems. The Hollywood system treats low pH mine drainage with hydrated lime and polymer and metals are settled in a concrete clarifier. The Brandy Camp system treats low pH mine drainage with hydrogen peroxide, polymer, and lime slurry and metals are settled in a series of ponds followed by a wetland.

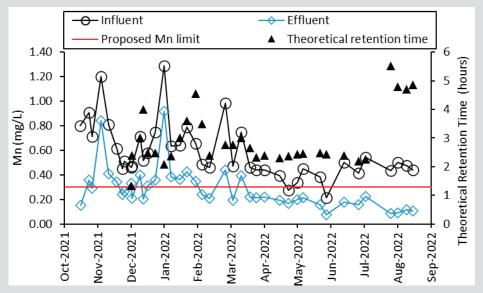
The pilot scale units were above ground, steel roll off containers. Hollywood unit contained 33 t of Mn oxide coated limestone from an operational passive Mn removal system (Fig. 1). The aggregate gradation was AASHTO #3 (AASHTO 2013), which has an average particle diameter of 38 mm and a calculated surface area of 0.72 cm<sup>2</sup>/g (calculated using Cravotta 2021). The Brandy Camp pilot contained 11 tonnes of limestone from a local limestone quarry. The aggregate gradation was AASHTO #8, which has an average particle diameter of 7 mm and calculated surface of 4.44 cm<sup>2</sup>/g (Cravotta 2021). Experiments were conducted by varying flow rates and measuring influent and effluent chemistry.

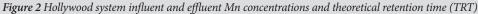
The Hollywood unit received circumneutral water containing an average 0.6 mg/L dissolved Mn and 1.5 mg/L particulate Fe and was operated for 10 months from November 2021 to August 2022. The Brandy Camp unit received circumneutral water containing an average 5.8 mg/L dissolved Mn and 1.7 mg/L particulate Fe and was operated for 12 months from 2022 to June 2023. Both systems decreased Mn to less than 0.3 mg/L Mn. However, the kinetics of Mn removal, determined from changes in Mn concentration and theoretical retention times, differed substantially.



*Figure 1* Hollywood pilot scale system in a 23 m3 roll off container. The Brandy Camp pilot system was similar but an 8 m3 roll off container

The Hollywood system operated at 2 to 5 hour retention times and Mn concentrations were decreased by about 0.3 mg/L regardless of flow rate (Fig. 2). Effluent Mn concentrations varied with influent Mn concentrations and were not consistently less than 0.3 mg/L. The system exhibited first order Mn removal kinetics, similar to abiotic, physio-chemical Mn removal kinetics (Morgan, 2005).





The Brandy Camp system operated at 1 to 4 hour retention times and except for startup and immediately after changes (e.g. dramatic increase in flow rate, restarting after drained empty), regularly decreased Mn concentrations to less than 0.3 mg/L (Fig. 3). The system was operated without interruption for 180 days (two months in fall 2022 and three months in spring/summer 2023). During these 180 days of operation, the average effluent concentration was 0.10 mg/L Mn. The system exhibited pseudo-zero order Mn removal kinetics, similar to biological Mn removal kinetics (Zhang et al. 2002).

The Brandy Camp pilot unit removed Mn to a lower concentration and at a faster rate compared to the Hollywood pilot unit. Both the physical and biological differences of these systems are likely important. Physically, the Brandy Camp unit contained smaller aggregate with about five times more surface area than the Hollywood pilot system or other full-scale passive systems. Biologically, the Brandy Camp unit was preceded by a wetland which may provide nutrients to microbes involved in Mn removal whereas the Hollywood unit was preceded by a concrete clarifier.

The rapid and consistent removal of Mn by the Brandy Camp system shows the opportunity for optimized passive removal of Mn. The Brandy Camp unit consistently met PADEP's 0.3 mg/L Mn effluent standard at 1/10<sup>th</sup> to 1/20<sup>th</sup> the retention time of existing passive treatment systems. These results suggest that passive treatment can play an important role in complying with lower Mn limits.

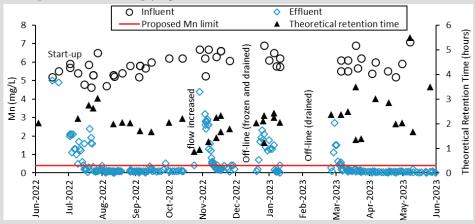


Figure 3 Brandy Camp system influent and effluent Mn concentrations and theoretical retention time

## Acknowledgements

This study was funded by a Pennsylvania Growing Greener award to the Western Pennsylvania Conservancy. The authors thank staff from the Pennsylvania Department of Environmental Protection, United States Geological Survey, and U.S. Department of the Interior Office of Surface Mining Reclamation and Enforcement for assistance with the design and operation of the pilot scale unit and data interpretation.

## References

AASHTO, American Association of State and Highway Transportation Officials (2013) Standard Specifications for Transportation Materials and Methods of Sampling and Analysis, 33rd edition. Washington D.C.

Burgos, W.D. (2021) Review of Manganese removal technologies from coal mining-associated waters and evaluation of the corresponding costs to coal mining industry. 44 pp. https:// files.dep.state.pa.us/PublicParticipation/ Public%20Participation%20Center/ PubPartCenterPortalFiles/Environmental%20 Quality%20Board/2022/August%209,%20 2022/02\_7-553\_Mn\_Final/05c\_7-553\_Mn\_ Final\_PSU%20report.pdf

- Cravotta, C.A. (2021) Interactive PHREEQ-N-AMDTreat water-quality modeling tools to evaluate performance and design of treatment systems for acid mine drainage. Applied Geochemistry 126, 1–19.
- Luan, F., Santelli, C.M., Hansel, C.M., Burgos, W.D. (2012) Defining manganese(II) removal processes in passive coal mine drainage treatment systems through laboratory incubation experiments. Applied Geochemistry 27, 1567–1578.
- Means, B.P., Rose, A. (2005) Rate of Manganese Removal in Limestone Bed Systems, 2005 National Meeting of the American Society of Mining and Reclamation. Proceedings America Society of Mining and Reclamation, Breckenridge, CO, pp. 702–717.
- Morgan, J.J. (2005) Kinetics of reaction between O2 and Mn(II) species in aqueous solutions. Geochem. Cosmochim. Acta 69: 35–48
- Pennsylvania Department of Environmental Protection Bureau of Clean Water (2020a) Water Quality Standard for Manganese and Implementation. Pennsylvania Bulletin 50(30): 3724-3733
- Pennsylvania Department of Environmental Protection Bureau of Clean Water (2020b) Rationale: Development of the Human

Health Criterion for Manganese. https:// files.dep.state.pa.us/PublicParticipation/ Public%20Participation%20Center/ PubPartCenterPortalFiles/Environmental%20 Quality%20Board/2019/December%2017/7-553\_WQS\_Mn\_Proposed/05\_7-553\_WQS\_ Mn\_Proposed\_Rationale.pdf

- Santelli, C.M., Pfister, D.H., Lazarus, D., Sun, L., Burgos, W.D., Hansel, C.M. (2010) Promotion of Mn(II) oxidation and remediation of coal mine drainage in passive treatment systems by diverse fungal and bacterial communities. Appl Environ Microbiol 76, 4871–4875.
- Santelli, C.M., Webb, S.M., Dohnalkova, A.C., Hansel, C.M. (2011) Diversity of Mn oxides produced by Mn(II)-oxidizing fungi. Geochemica et Cosmochimica Acta 75, 2762–2776.
- Tan, H., Zhang, G., Heaney, P.J., Webb, S.M., Burgos, W.D. (2010) Characterization of manganese oxide precipitates from Appalachian coal mine drainage treatment systems. Applied Geochemistry 25, 389-399.
- Zhang, J., Lion L.W., Nelson Y., Shuler M.L., Ghiorse W.C. (2002) Kinetics of Mn(II) oxidation by Leptothrix discophora SS1. Geochem. Cosmochim. Acta 65: 773–781