

Comments in response to proposed rulemaking by the Environmental Quality Board [25 PA.CODE CHS. 92 AND 96] regarding Water Quality Standard for Manganese and Implementation [50 Pa.B. 3724] [Saturday, July 25, 2020].

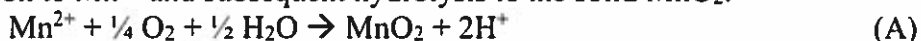
Submitted by Robert S Hedin, September 15, 2020

My comments address the technical feasibility of achieving the proposed standard. My understanding of this matter is based on my experience as a research ecologist at the US Bureau of Mines (Department of Interior) 1986-1994 and as owner of Hedin Environmental since 1994.

The proposed rulemaking would lower effluent limits for Mn to 0.3 mg/L. This is a substantial decrease from current mining permit limit of 2.0 mg/L (monthly average) and the instream standard of 1.0 mg/L. As an active member of the mine water community in PA, I have become aware of concerns that this limit can not be economically achieved. My comments address that concern and draw on my experiences in PA and at mine sites around the world.

Removal of Mn from Water

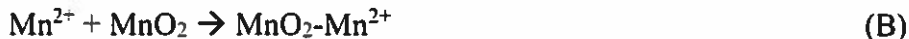
Mn is present in water as a divalent dissolved cation, Mn^{2+} , that is conventionally removed by oxidation to Mn^{4+} and subsequent hydrolysis to the solid MnO_2 .



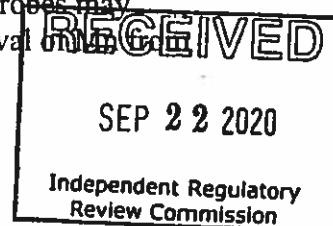
The oxidation of Mn^{2+} is the slowest part of the reaction. The oxidation does not occur at low pH, so the treatment of acidic waters requires the addition of an alkaline reagent such as NaOH, $Ca(OH)_2$, or $NaCO_3$.

Mn^{2+} oxidation occurs by two distinct chemical processes. The homogeneous process occurs by reaction (A) and requires a pH above 9 which is achieved through the addition of caustic chemicals, most commonly sodium hydroxide (NaOH). Most conventional Mn-removing treatment systems in PA promote the homogeneous oxidation reaction using NaOH. The process creates voluminous sludge which must be managed and disposed of. It is common for the effluent of these systems to have pH > 9, which can be ecologically problematic. This technology is proven for meeting the current 2.0 mg/L standard for most mine sites. Using this method to reliably produce an effluent with 0.3 mg/L Mn will be challenging and will likely create alternative problems such as high pH and increased sludge management challenges.

Mn oxidation also occurs by a heterogeneous process that involves oxidation of Mn^{2+} that has been adsorbed onto a solid. In mine water systems, the most common solid is previously formed MnO_2 and the reaction is as follows.



The heterogeneous reaction occurs at circumneutral pH and the solids produced are dense. The presence of MnO_2 speeds the reaction and thus acts as a catalyst. This is the natural process that occurs widely in soils and streams. Many streambeds in mining-impacted areas of PA have black substrate due to the natural formation of MnO_2 . It is suspected that microbes may contribute to the oxidation of Mn^{2+} under these conditions. The natural removal of Mn is



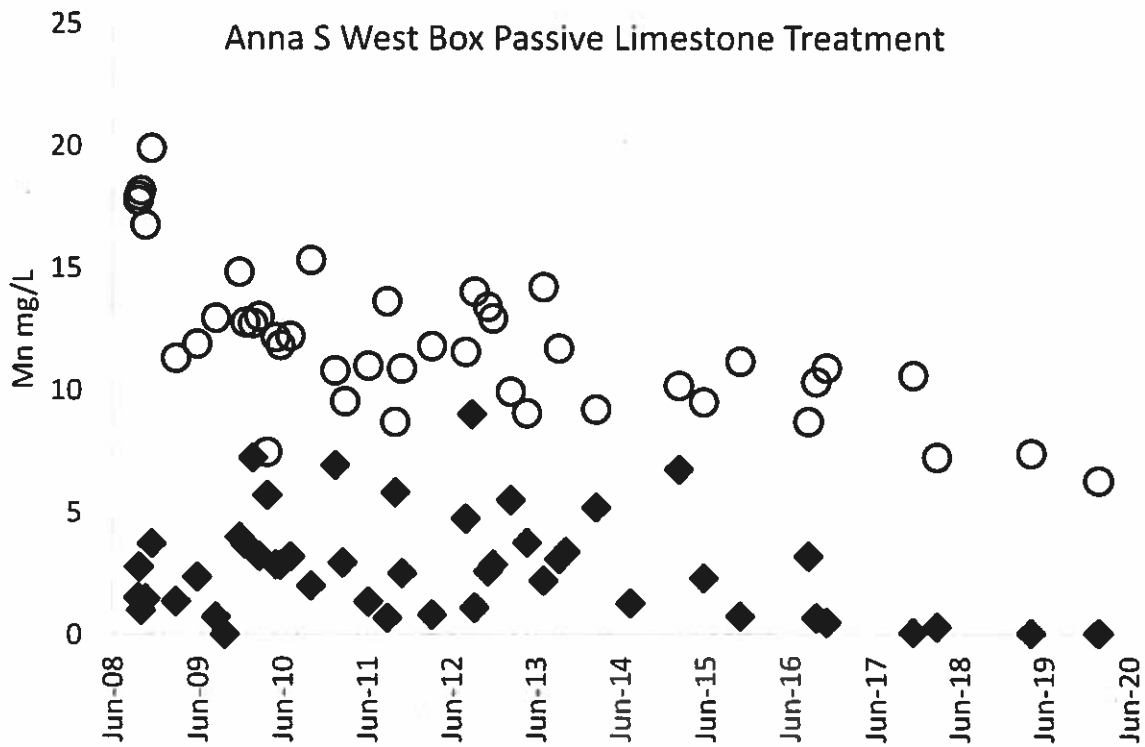
water likely occurs by a combination of microbial and abiotic heterogeneous processes with the net effect being that Mn is removed at lower pH than occurs with the homogeneous reaction.

Passive mine water treatment systems utilize the heterogeneous process. Passive systems contain physical substrates that provide points of attachment for solids and microbes that subsequently catalyze the Mn removal process. The two most common substrates are wetlands and aggregate. The use of constructed wetlands for Mn removal was pioneered in the 1980's and 1990's. The approach is effective, but the results can be variable due to changing redox conditions and flow paths in the wetlands. Aggregate has proven to be a more reliable substrate. In PA, where mine water is often acidic, limestone aggregate is typically used. However, in areas where the water is alkaline and limestone is not available, non-calcareous aggregates have been used with similar Mn-removing success.

This opinion will focus on the oxic aggregate-based passive treatment systems. The results of four systems are presented. All the systems contain limestone beds that are open to the atmosphere and designed to promote oxic conditions. The systems treat waters containing a variety of contaminants, but the focus here is on Mn.

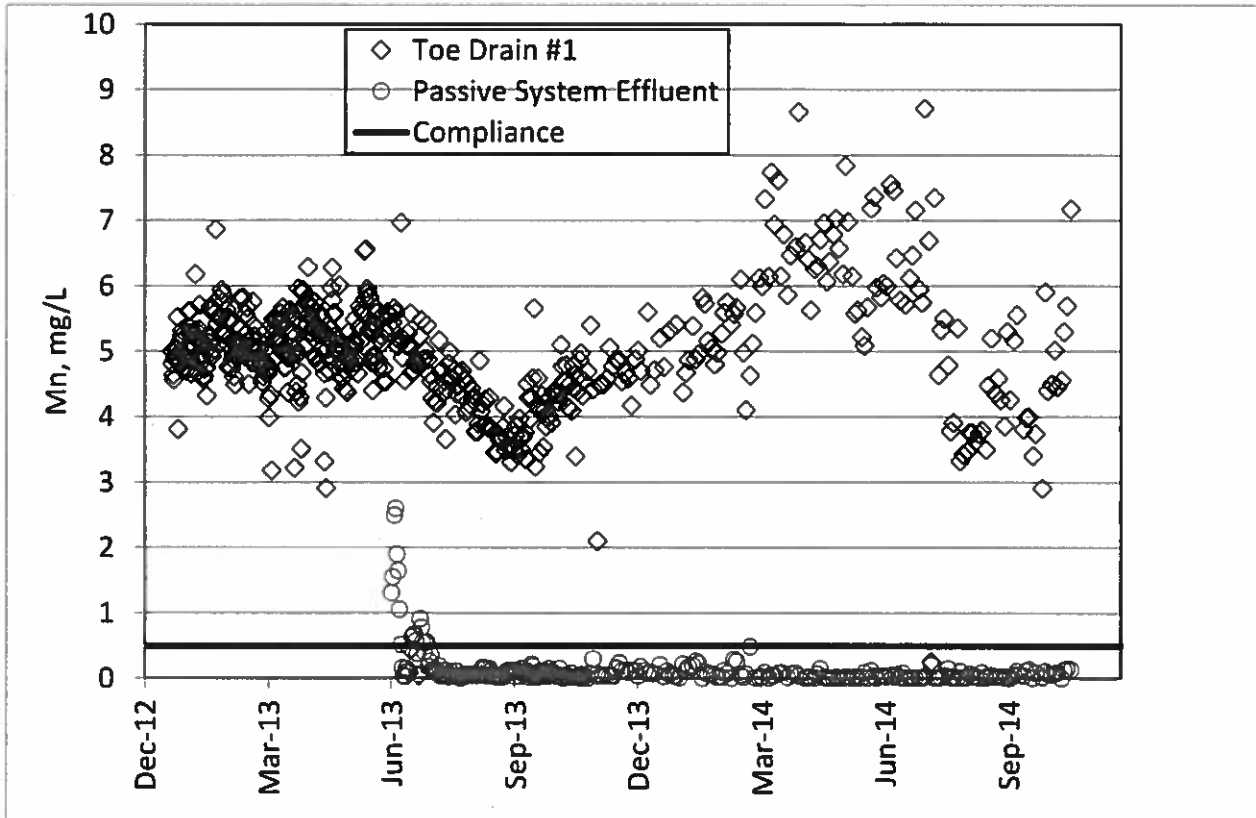
Mitchell West Box, Tioga County PA

An experimental oxic limestone treatment bed was installed at the Anna S Mine in 2008 as part of DEP-funded research project. The system consists of limestone aggregate in a roll-off container that is plumbed to receive acid mine drainage from the Mitchell Mine. The passive system is still operating and is maintained by the Babb Creek Watershed Association. While the research was focused on treatment of acidity, Al and Fe, sustainable removal of Mn has also been observed (graph below). Over the last four years of treatment, the effluent Mn concentrations have been ≤ 0.5 mg/L and three measurements have been less than 0.3 mg/L.



Phu Kham, Laos

Copper mining at the Phu Kham mine in Laos created a discharge from a tailings facility that is alkaline with 3-8 mg/L Mn. The effluent limit is 0.5 mg/L. A passive system consisting of a large bed of granite aggregate was installed. Influent and effluent concentrations of Mn are shown below. After a six week start-up period, the system consistently produced a final effluent with < 0.5 mg/L Mn. 90% of the effluent samples have contained < 0.3 mg/L Mn.



Summary

Data from a variety of sites indicate that passive treatment designs that promote the heterogeneous and microbial removal of Mn can reliably produce final effluents with less than 1.0 mg/L Mn and, in many cases, less than 0.3 mg/L Mn. Sustaining such treatment requires maintenance as the aggregate must be periodically stirred and cleaned. These efforts typically occur on a multi-year schedule and the costs are minor. It is likely that sustaining effluents with <0.3 mg/L Mn would require more frequent maintenance, but not to a degree that substantially erodes the attractive economics of the treatment approach.

The ability of oxic aggregate beds to sustainably produce effluents with < 0.3 mg/L Mn is uncertain but, based on the information available from these four sites and many other passive systems in PA, it is achievable. Many effluent samples with < 0.3 mg/L Mn have been collected from these systems. If the Commonwealth implements the new Mn standard, it should also support research efforts to optimize passive Mn-removing treatment processes and develop BMPs for operation & maintenance of systems.

Lastly, a common criticism of passive treatment is that the systems are too large and cannot be accommodated by available space. The passive treatment of Mn contained by large deep mine discharges (>1000 gpm) may require large aggregate beds that cannot be accommodated on the mine sites by gravity flow systems. In these cases, pumping of water to a suitable site will need to be considered. Pumping is never preferred, but the combination of pumping with highly effective passive treatment is likely less expensive and more effective for Mn removal than standard chemical treatment alternatives. If the Commonwealth implements the new Mn standard, it should support research that determines the comparative costs and effectiveness of conventional chemical treatment, aggregate-based passive treatment, and aggregate-based passive treatment with pumping.

Robert S Hedin, PhD

President
Hedin Environmental
195 Castle Shannon Blvd
Pittsburgh PA 15228