

# Enhanced Mn Treatment in Mine Drainage Using Autocatalysis in a Steel Slag-Limestone Reactor

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**Abstract** Modified steel slag and Mn sand reactors were operated for one year to remove Mn. The steel slag reactor showed the lowest Mn, below 0.2 mg/L, but Mn increased above 2.7 mg/L at only 4.5 mg/L of Fe. In contrast, a reactor consisting of steel slag and limestone, after accumulating autocatalytic Mn (hydr)oxides for 160 bed volumes, brought Mn to below 2 mg/L from an initial concentration of 30–50 mg/L, and produced outflow with the lowest pH of 7–9. The reactor also maintained Mn below 3.0 mg/L, even when loaded with 17.7 mg/L of Fe.

**Key words** Manganese, Autocatalysis, Steel slag, Birm, Passive Treatment

## Introduction

Passive Mn treatment is challenging because precipitation of (hydr)oxides requires high pH (usually >9.0) and the existence of Fe can inhibit Mn removal because Fe is precipitated prior to Mn (Nairn and Hedin 1993). The slag leach bed (SLB) method has recently been applied due to fewer Fe interaction and clogging effects (Ziemkiewicz 1998; Hamilton et al. 2007; Skousen et al. 2017). In this method, freshwater reacts with the steel slag and flows into a pH adjustment pond. However, it is generally difficult to control the flow rate of the alkaline water from the SLB and efficiently maintain good water quality at discharge (Goetz and Riefler, 2014).

The surfaces of manganese (hydr)oxides can act as an autocatalyst for the oxidation of dissolved  $Mn^{2+}$  ions. The proposed mechanism for the destabilization of  $Mn^{2+}$  ion symmetry is the exchange of  $H_2O$  ligands between hydrated  $Mn^{2+}$  ions and the surfaces of manganese (hydr)oxides (Morgan 2000). Therefore, the  $Mn^{2+}$  oxidation rate generally increases in the presence of manganese (hydr)oxides (Coughlin and Matsui 1976; Barloková and Ilavský 2009; Younger et al. 2002).

The application of a slag reactor could be cost-effective, while maintaining a stable and low Mn concentration and pH, if it is tolerant to Fe and removes Mn efficiently at pH <9.0. Therefore, the objective of this study is to evaluate modified slag reactors that use autocatalysis, are Fe tolerant, and maintain a relatively low pH discharge.

## Methods

Five reactors were chosen to remove Mn, three were filled with alkaline media (steel slag, steel slag+limestone, and steel slag+Mn-coated gravel), one was filled with catalytic media (Mn-coated sand), and the last was a control, filled with filter agent (Table 1; Fig. 1). The three reactors with alkaline media had an upward flow, while the other two reactors had a downward flow. Retention time was calculated by dividing the effective pore volume by flow

rate. A layer of 4–5 cm diameter gravel was installed at the bottom of each reactor to create uniform flow. The diameters of the steel slag, limestone and Mn-coated gravel were 2–6 mm, 2–5 cm, and 2–5 cm, respectively.

**Table 1** Reaction media and reactor pore volumes.

Reactor	Alkaline media			Catalytic media and control	
	S	SL	SG	B	FA
Composition	Steel slag (100%)	Steel slag (40%) + Limestone (60%)	Steel slag (40%) + Mn-coated gravel (60%)	Mn-coated sand (Birm®)	Filter agent (Filter-Ag®)
Pore volume	4.40	4.60	4.05	5.34	5.80
Reactor volume	12.7	12.7	12.7	12.1	12.1
Porosity	0.35	0.36	0.32	0.44	0.48

(a)



(b)



**Figure 1** (a) Mn removal reactors after 120 days (S, SL, SG, B and FA from left to right) and (b) Mn precipitates on the surface of Mn-coated gravel (left) and limestone (right) after reactor operation.

To coat the gravel with Mn, 3.6 L of 3%  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  solution was injected into 24 L of white gravel, followed by the addition of 1.8 L of 3%  $\text{KMnO}_4$  solution. The excess solution was discarded after reaction, and the gravel dried at room temperature. The reaction and drying process was repeated twice and the resulting Mn-coated gravel was rinsed with water and air dried prior to use. Birm® (B), 0.5–2.0 mm in diameter, and Filter-Ag® (FA), 0.7–2.0 mm in diameter, produced by Clack Corporation were used as the Mn-coated sand and filter agent, respectively.

The three reactors with alkaline media were operated for 366 days and the B and FA reactors were operated for 303 days. Initial inflow Mn concentrations were 30–50 mg/L and 2–10 mg/L for the alkaline media and other reactors, respectively. Retention times were 0.6–1.8 d and 0.5–3.3 d within the alkaline media and other reactors, respectively.

After the reactions with Mn alone, Fe plus Mn were added to the inflow for 26 additional days. Fe concentrations of 4.5–24.4 mg/L, with  $\text{Fe}^{2+}$  of 1.2–12.0 mg/L, and 0.7–28.7

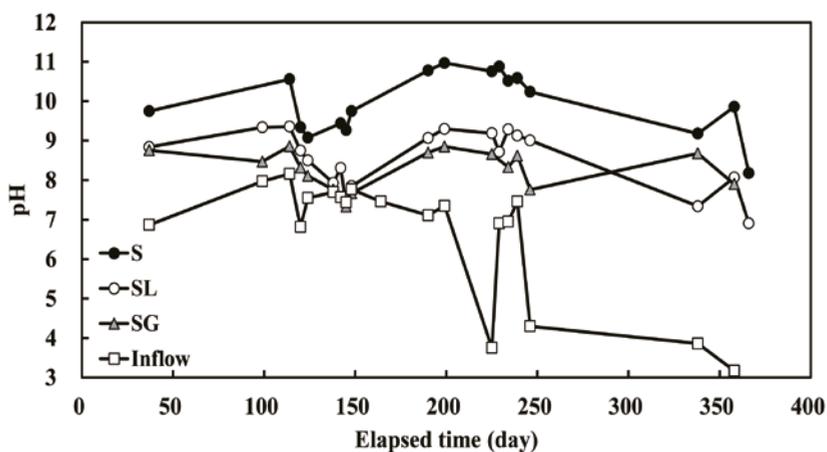
mg/L, with  $\text{Fe}^{2+}$  of 0.3–17.4 mg/L, were added to the alkaline media and other reactors, respectively. Mn concentrations of 32–46 mg/L and 6–11 mg/L were added to the alkaline media and other reactors, respectively. Retention times were respectively 0.8–1.5 d and 1.3–1.9 d in the alkaline media and other reactors.

Dissolved  $\text{Fe}^{2+}$  concentrations in the water samples were determined using a portable colorimeter (model Hach DR-890) following the phenanthroline method (APHA 1998). pH was measured using a portable meter (model Orion 3 Star). Water samples were filtered through a 0.45- $\mu\text{m}$  membrane and then transferred into 50-mL PE tubes. Samples for cation analysis were preserved by adding ~10 drops of concentrated nitric acid to maintain the pH <2, and then stored at 4°C until analysis. Concentrations of dissolved cations were analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Varian 720-ES) at the Institute of Mine Reclamation Technology, Korea Mine Reclamation Corporation. Relative standard deviations were less than 5% of the measured values for ICP-OES.

## Results and discussion

### Reactors with alkaline media

Results from the steel slag (S) reactor, filled only with slag, showed that the pH at the outflow varied between 9.0 and 11.0 for nearly all samples (Fig. 2). The pH range for outflow from the steel slag with limestone (SL) and steel slag with Mn-coated gravel (SG) were 8.0–9.5 and 8.0–9.0, respectively. The slightly higher pH in the SL outflow than in the SG may have been due to pH buffering by the carbonate against pH decrease from dissolution of atmospheric  $\text{CO}_2$ . The outflow pH and Ca concentrations from all three reactors with alkaline media did not show a decreasing trend over time when compared to the inflow. Furthermore, outflow Mn concentration did not indicate an increasing trend, and the Mn removal rate (mg/d) did not show a decreasing trend (Fig. 3).



**Figure 2** Inflow and outflow pH for the S, SL, and SG reactors as a function of elapsed time.

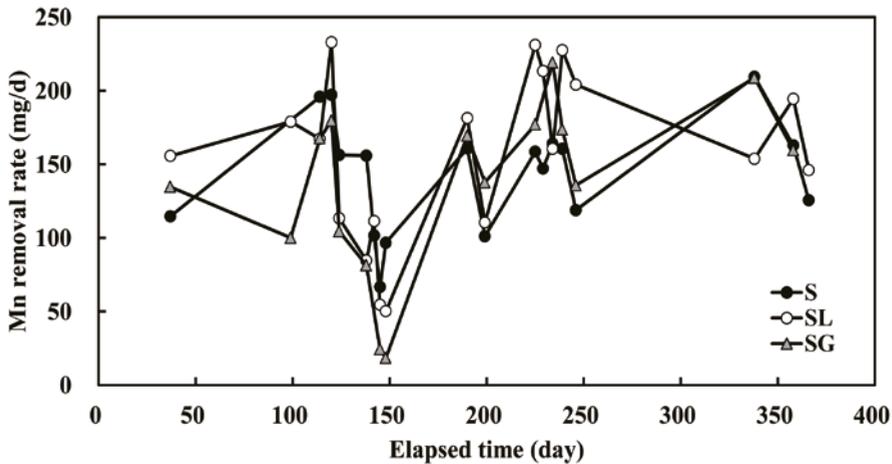


Figure 3 Mn removal rate at the outflow from the S, SL, and SG reactors as a function of elapsed time.

The relationship between pH and Mn of outflow at specific periods (<200 d, 200–300 d and >300 d) showed that Mn removal was impacted by increasing pH and elapsed time (Fig. 4). The S reactor showed Mn concentrations below 0.2 mg/L with a pH above 9.0, with the exception of one sample (pH 8.2). However, Mn also decreased after ~200 d (~160 bed volumes) at pH ≤~9 for SL and SG. Most Mn concentrations were 1–20 mg/L until 200 d and then subsequently decreased to 0.1–2 mg/L after. This suggests an enhancement in autocatalytic oxidation by accumulating Mn (hydr)oxides (Fig. 1b). Thus, Mn concentrations of 30–50 mg/L can be decreased to <2 mg/L with a removal ratio of ~95% at pH ≤9, possibly by gradually increasing autocatalysis. This lower pH at the reactor outflow mostly meets the pH requirements (≤9) of the EPA treatment standard (USEPA 2010).

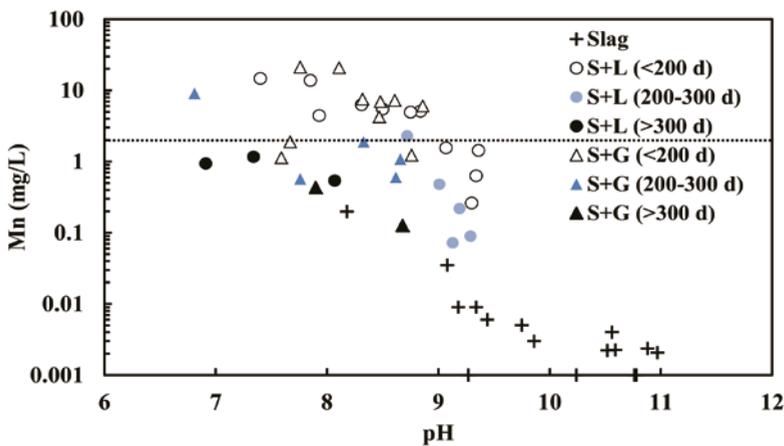
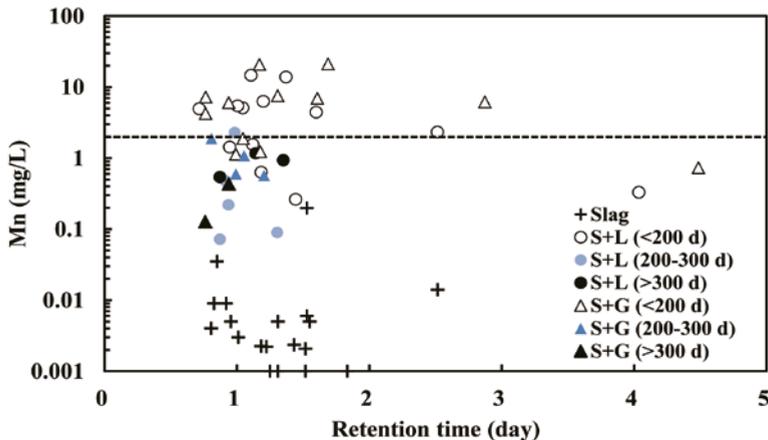


Figure 4 Variation in Mn concentrations with pH for specific reactions time periods for the S, SL, and SG reactors.

Mn concentrations decreased after ~200 d even at similar retention times, and were similar to the observations of the pH-Mn relationship (Fig. 5). When the <200 d reaction times are included, required retention times seem to be 3 d and 4 d for the SL and SG, respectively. However, the required retention time decrease to ~1 d after ~200 d.



**Figure 5** Variation in Mn concentrations with retention time for specific reaction time periods for the S, SL, and SG reactors.

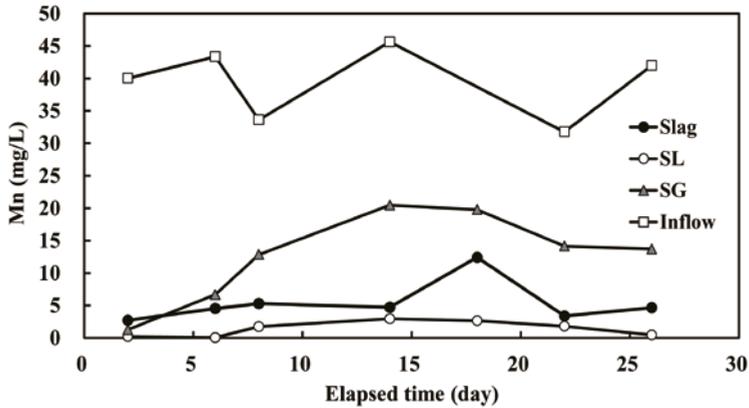
#### Reactors with catalytic media

The B and FA reactors increased the pH by 1.0–1.5 and 0.5, respectively, and also increased Ca concentrations by 20–80 mg/L and 0–50 mg/L, respectively; these results suggest that the dissolution of Ca compounds increased the pH in the outflow from the B reactor. Mn concentrations in the outflow from the B reactor were consistently below 0.024 mg/L, removing most of the 2–10 mg/L from the inflow. Catalytic oxidation was the likely cause, as the minimum outflow pH was as low as 8.4. The FA reactor, the control, generally could not remove >2 mg/L of Mn.

#### Treatment efficiency after addition of Fe

Tolerance to Fe was evaluated in all reactors. Fe addition resulted in changes to the outflow pH from the alkaline media reactors; the pH decreased to 7.0–8.0 from 7.5–11.0, possibly due to formation of iron hydroxides. The addition of Fe at 0.7–28.7 mg/L in the inflow was almost exhausted to <0.05 mg/L in the outflow. The SG and S reactors had outflow with Mn at 6.7–20.4 mg/L and 2.7–12.4 mg/L, respectively (Fig. 6). Mn exceeded 2 mg/L even with Fe at <5 mg/L for both the S and SG reactors. In contrast, the SL reactor showed Mn consistently less than 3.0 mg/L, even with Fe concentration at 17.7 mg/L.

The principle mechanisms for satisfactory Fe tolerance is likely a combination of the following: the autocatalytic oxidation of Mn and Fe by accumulated Mn (hydr)oxides on the surface of limestone, Fe removal by limestone, and transformation of  $\text{Mn}^{2+}$  into  $\text{MnCO}_3$  supplied from carbonate ion and subsequent oxidation, even in the presence of Fe.



**Figure 6** Variation in Mn concentrations as a function of elapsed time since Fe addition for the S, SL, and SG reactors.

For the B reactor, Mn was maintained at  $<0.3$  mg/L and pH was 7.6–8.6 in the outflow. This indicates catalytic oxidation of Mn was effective, at least for Mn concentrations between 6 and 11 mg/L in the inflow.

## Conclusions

Although the S reactor, filled with only steel slag, showed the lowest Mn concentrations,  $<0.2$  mg/L, the outflow had the highest pH of 9–11, which requires lowering to meet effluent standards. Furthermore, Mn concentrations increased above 2.7 mg/L even with 4.5 mg/L of added Fe. In contrast, the SL reactor, with steel slag and limestone, removed Mn from 30–50 mg/L to below 2 mg/L and had a pH of 7–9 after accumulation of Mn (hydr)oxides for ~200 d (160 bed volumes). This may have been due the enhancement of auto-catalysis by the accumulated Mn (hydr)oxides. The SL reactor also maintained favorable efficiency even with high Fe concentrations. The B reactor, filled with Birm<sup>®</sup> with inflow Mn of  $<12$  mg/L, also showed low Mn concentrations of  $<0.024$  mg/L and  $<0.3$  mg/L, without and with Fe addition, respectively. However, in contrast to the manufactured B reactor, the application of SL provides the additional benefit of recycling waste material (steel slag).

## Acknowledgements

This work was supported by the Korea Mine Reclamation Corporation funded by the Korean Government Ministry of Trade, Industry, and Energy.

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