Steel Slag-Limestone Reactor with Resistance to Fe: Laboratory and Pilot Scale Evaluations of Mn Treatment Efficiency

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Abstract

Mixed substrate of steel slag and limestone were applied in reactors to evaluate resistibility to Fe. Steel slag mixed with limestone could decrease Mn from 32–46 mg L^{-1} to <3 mg L^{-1} with addition of 4.5–24.4 mg L^{-1} of Fe in the bench-scale experiment. In the pilot-scale experiments in five mines in South Korea, 95–99% of Mn was removed during the maximum test period of 4 years. Precipitation as Fe and Mn carbonates may have contributed to the Mn removal and resistibility to Fe.

Keywords: Manganese, Passive Treatment, Mine Drainage, Mn Carbonates, Fe Resistibility

Introduction

Mn is one of the common contaminants in mine drainage. Mn in drinking water has been found to affect the nervous system (USEPA 2004; Rodríguez-Barranco *et al.* 2013), and it has been associated with intellectual impairment in school-aged children (Bouchard *et al.* 2011; Rodríguez-Barranco *et al.* 2013). To remove Mn in mine drainage, pH higher than 9.5 is often required, so active treatment has been generally applied.

Slag leach beds (SLBs) have been applied in pilot- and full-scale passive treatment systems of Mn in the last 25 years (Ziemkiewicz 1998; Hamilton *et al.* 2007; Skousen *et al.* 2017 and references therein). In this method, freshwater reacts with steel slag to generate alkaline water to treat Mn-bearing water at downstream. However, it is generally difficult to meet environmental standards for Mn and pH at the effluent due to the changing flow rate of the alkaline water and contaminated water (Goetz and Riefler 2014). As an alternative of SLBs, a slag reactor containing steel slag to directly react with contaminated water can be used. Two issues need to be overcome to apply a slag reactor. One is clogging of the substrate, which can induce overflow; this can be improved by applying a stop-log to decrease the outflow water level and induce a sufficient hydraulic gradient. The other one is that Fe^{2+} of the influent inhibits Mn removal due to the prior oxidation of Fe^{2+} (Nairn and Hedin 1993; Gouzinis *et al.* 1998) and/or reductive dissolution of Mn oxides by Fe^{2+} (Burdige *et al.* 1992; INAP 2012).

Development and assessment of passive Mn treatment system with tolerance of Fe is limited. The objective of this study is to evaluate Fe-tolerance in some kinds of slag reactor, to assess the mechanism, and to assess Mn treatment efficiencies of several pilot-scale slag reactors.

Materials and methods

In the bench-scale experiment, S, SL, and SG reactors were filled with steel slag, steel slag (40 vol.%) + limestone (60%), and steel slag (40%) + Mn-coated gravel (60%), respectively. Steel-making slag from a basic oxygen furnace of a steelmaking factory in South Korea was used. It had CaO, SiO_2, Fe oxides, MgO, Al_2O_3, MnO, and P_2O_5 contents of 29.4%, 15.0%, 27.8%, 6.9%, 3.5%, 3.4%, and 2.1%, respectively. The diameters of the steel

slag, limestone and Mn-coated gravel were 2–6 mm, 2–5 cm, and 2–5 cm, respectively. The manufacturing procedure of the Mn-coated gravel is described in Kim *et al.* (2017). A layer of 4–5 cm diameter gravel was installed at the bottom of each reactor to create uniform upward flow.

The three reactors were operated for 366 days. Initial inflow Mn concentrations were 30–50 mg L^{-1}, and residence times were 0.6–1.8 d. After the reactions with Mn alone, both Fe and Mn were added to the inflow for 41 additional days. Fe, Fe^{2+}, and Mn concentrations were 4.5–24.4 mg L^{-1}, 3.1–12.0 mg L^{-1}, and 32–46 mg L^{-1}, respectively, and residence times were 0.8–1.5 d at that time.

Pilot-scale treatment systems were installed and operated in Ilwol, Dalseong, Dadeok, Sambong, Taehwa, and Sindong mines in various regions in South Korea. Inflow Mn concentrations ranged between 2 and 45 mg L^{-1} and operation periods ranged between 0.5 and 4 years.

The pH values were measured using a portable meter (model Orion 3 Star). Dissolved Fe^{2+} concentrations in the water samples were determined using a portable colorimeter (model Hach DR-890) following the phenanthroline method (APHA 2017). Alkalinity was determined in the field via volumetric titration using a digital titrator (model Hach AL-DT, Hach). Water samples were filtered through a 0.45-μm 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 (IMRT), Korea Mine Reclamation Corporation. Relative standard deviations were less than 5% of the measured values for ICP-OES. Precipitates in the SL reactor were analyzed via scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), Carl Zeiss Supra40) at IMRT.

Results and discussion

Mn treatment efficiency and resistibility to Fe in bench-scale experiment

Tolerance to Fe was evaluated in all reactors in the bench-scale experiment. The operation period and discussions were added from the previous study (Kim *et al.*, 2017). Outflow pH from the reactors increased to 6.9–7.8 from 3.1–5.0. The Fe concentrations at 4.5–24.4 mg L^{-1} in the inflow were almost exhausted to <0.05 mg L^{-1} in the outflow. The S (slag) and SG reactors had outflow with Mn at 2.7– 12.4 mg L^{-1} and 1.2–29.0 mg L^{-1}, respectively (Fig. 1). Mn exceeded 2 mg L^{-1} even with Fe at <5 mg L^{-1} for both the S and SG reactors. In contrast, the SL reactor showed Mn consistently less
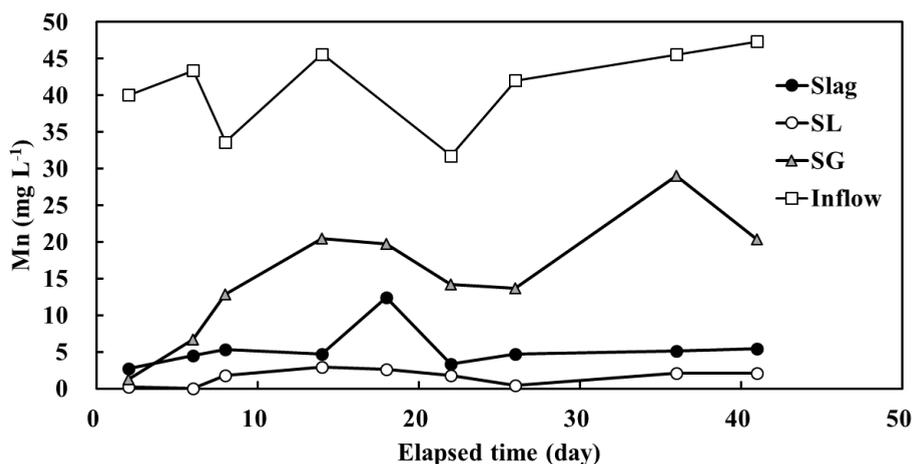

Figure 1 Variation in Mn concentrations as a function of elapsed time since Fe addition for the S, SL, and SG reactors.
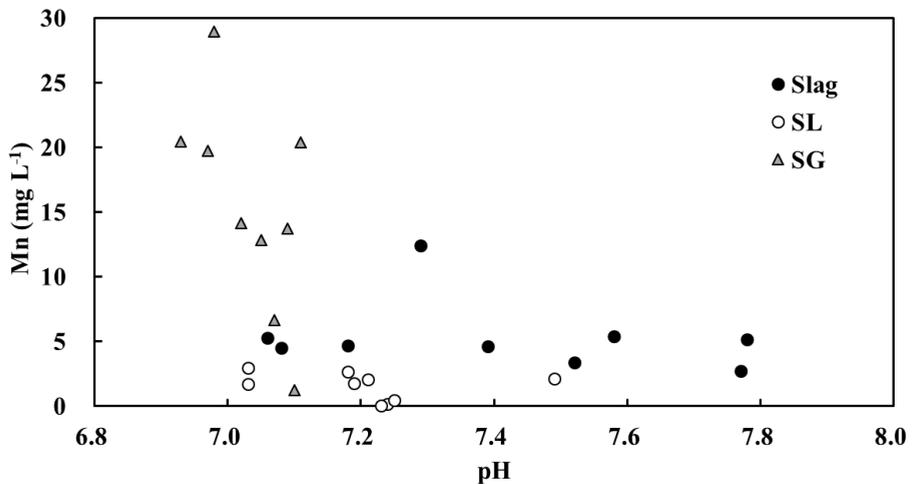
Figure 2 Plot of Mn concentrations against pH after the Fe addition for the S, SL, and SG reactors.
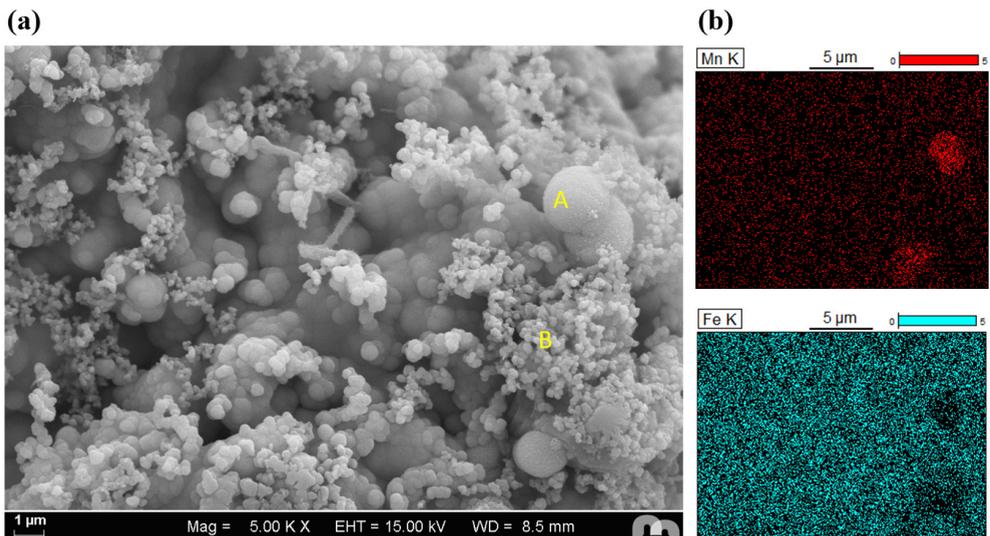

Figure 3 (a) An SEM image of Mn and Fe compounds on the surface of the limestone in the SL reactor (5000x) and (b) EDS mapping results for Mn and Fe.

than 3.0 mg L^{-1}, even with Fe concentration at 24.4 mg L^{-1}. In the plot of Mn concentrations against pH (Fig. 2), SL reactor also showed lower Mn concentrations than S and SG reactors in similar pH condition.

Precipitates on the surface of limestone were collected from the SL reactor and analyzed by using SEM and EDS (Fig. 3 and Table 1). There were several spheres and aggregates which were enriched in Mn and Fe, respectively (Fig. 3a and b). Analysis re-

sults from EDS showed that carbon was also enriched in both A and B positions (Table 1), which indicates Mn and Fe carbonates. Therefore, Mn and Fe could be also present as carbonates in the SL reactor, which will be oxidized eventually to Mn oxides such as MnOOH and MnO$_2$. Thus, carbonates may help the effective removal of Mn even in the presence of Fe. Luan (2012) also reported precipitation of Mn as carbonate in treatment facilities using limestone.

Table 1 EDS analysis results for precipitates at the surface of the limestone in the SL reactor. Positions A and B are indicated in Fig. 3a.

Element	Proportion (atomic %)	
	Position A	Position B
Mn	21.05±0.22	1.77±0.13
Fe	1.67±0.18	12.36±0.20
C	11.38±0.21	9.49±0.62
O	57.37±0.53	61.18±0.45

Table 2 Mn treatment data from laboratory (bench) and pilot scale systems including slag reactor which consists of steel slag and limestone.

Mine	Lab.	Dadeok	Ilwol	Sambong	Sindong	Taehwa
Province	-	Gyeongsang-buk-do	Gyeongsang-buk-do	Gyeongsang-nam-do	Gangwon-do	Chungcheong-nam-do
Steel slag : Limestone (vol. ratio)	4:6, slag 100%	1:1	1:1	4:6	4:6	4:6
Avg. Mn removal efficiency	96%	95%	98%	98%	98%	99%
Avg. inflow Mn (mg L^{-1})	44	2	7	2	8	4
Avg. inflow pH	6.4 (3.2–8.2)	7.3	7.1 (6.1–7.9)	7.0 (6.8–7.7)	7.8 (6.6–8.5)	6.6 (6.5–6.7)
Avg. outflow pH	8.5 (6.9–9.4)	9.0	8.7 (7.9–10.2)	9.2 (8.8–9.7)	11.1 (9.7–11.8)	10.9 (10.6–11.1)
Test period (yr)	2	0.5	4	0.5	0.5	0.5

Accordingly, limestone could have enhanced Mn removal by carbonate formation on the surface (Franklin and Morse, 1983; Aziz and Smith, 1992; Hem and Lind, 1994; Bamforth *et al.*, 2006; Aguiar *et al.*, 2010; Silva *et al.*, 2012a, b). Moreover, presence of limestone may prevent localized pH decrease during Fe^{2+} oxidation to Fe hydroxides, which can help to maintain Mn removal efficiency and to prevent redissolution of Mn oxides.

Mn treatment efficiency in pilot-scale experiments

Pilot-scale passive treatment facilities including slag reactor which consists of steel slag and limestone were operated in five abandoned mines in South Korea (Table 2), which included three coal mines (Ilwol, Sindong, and Taehwa) and two metalliferous mines (Dadeok and Sambong). Especially, the slag reactor at the Ilwol mine removed 98% of the inflow Mn of 12 mg L^{-1} in average for four years (Fig. 4; Kim *et al.*, 2021). Although Mn oxides accumulated in the slag reactor, the increase in water level of the reactor could not be observed. The slag reactors at the other four mines (Dadeok, Sambong, Sindong, and Taehwa) also showed Mn removal efficiencies of 95–99% from the inflow of 2–8 mg L^{-1} during the operation period of 0.5 yr. Additionally, the slag reactor at the Sambong mine also removed Zn of 9 mg L^{-1} at the inflow due to the pH increase.
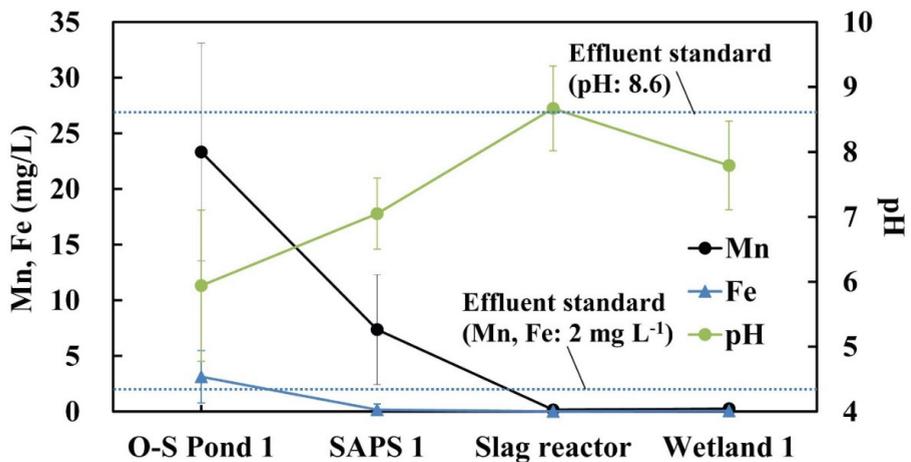
Figure 4 Average Mn and Fe concentrations and pH in the outflow from the pilot-scale treatment facilities for 281 days in the Ilwol mine. The error bars indicate standard deviations. The South Korean standards (for "clean" areas) for Mn (2 mg L^{-1}) and pH (8.6) are also indicated (Kim et al., 2021).

Conclusions

The reactor with mixed substrate of steel slag and limestone removed Mn from 32–46 mg L^{-1} to <3 mg L^{-1} even with the addition of 4.5–24.4 mg L^{-1} of Fe during the bench-scale experiment. Presence of limestone could maintain stable Mn removal efficiency possibly owing to carbonate formation on the surface and/or prevention of localized pH decrease during Fe^{2+} oxidation to Fe hydroxides. Pilot-scale slag-limestone reactors were recently operated in five mines in South Korea and 95–99% of Mn was removed during the maximum test period of 4 years.

Acknowledgements

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