Assessing Removal Efficiencies of Mn and Ni in Mine Drainage Using Bench- and Pilot-scale Slag Reactors and Design of Treatment System

Dae-gyu Im[1], Duk-min Kim[2], Hye-Lim Kwon[3], Joon-Hak Lee[4], Mi-Sun Park[5], Seong-Taek Yun[6]

[1]*Department of Earth and Environmental Sciences, Korea University, Anam-ro 145, Seongbuk-gu, Seoul, 02841, Republic of Korea, daegull1995@korea.ac.kr, ORCID 0000-0002-7499-8403*

[2]*Department of New Energy and Mining Engineering, Sangji University, Sangjidae-gil 83, Wonju, Gangwon-do, 26339, Republic of Korea, kdukmin8@sangji.ac.kr, ORCID 0000-0002-1537-6866*

[3]*Department of New Energy and Mining Engineering, Sangji University, Sangjidae-gil 83, Wonju, Gangwon-do, 26339, Republic of Korea, ossgpfla@naver.com*

[4]*Korea Mine Rehabilitation and Mineral Resources Corporation, Hyeoksin-ro 199, Wonju, Gangwon-do, 26464, Republic of Korea, jun292@komir.or.kr*

[5]*Korea Mine Rehabilitation and Mineral Resources Corporation, Hyeoksin-ro 199, Wonju, Gangwon-do, 26464, Republic of Korea, mspark@komir.or.kr*

[6]*Department of Earth and Environmental Sciences, Korea University, Anam-ro 145, Seongbuk-gu, Seoul, 02841, Republic of Korea, styun@korea.ac.kr*

Abstract

This study aimed to treat mine drainage containing Mn and Ni using a passive slag reactor. Bench-scale and pilot-scale experiments were conducted to optimize the residence time for the reactor and assess its effectiveness in removing pollutants. The generated precipitates from the reactor showed effective adsorptive removal of Ni. Pilot-scale experiments showed decreased Mn concentration over time, attributed to autocatalytic oxidation by MnO_2. The study suggests that a slag reactor with accumulating Mn oxides can be a promising technology for removing Mn and Ni. Furthermore, adding a precipitation tank can improve its long-term operation.

Keywords: Slag Reactor, Mn Oxide, Autocatalytic Oxidation, Passive Treatment of Mine Water

Introduction

Manganese and nickel are the water pollutants in mining areas and are the most challenging metals to remove. Typically, they are removed by large amounts of alkaline agents such as $Ca(OH)_2$ and $Na(OH)$ in (semi-) active facilities to increase the pH < 9. In the United States, SLB (Slag leach bed) has been applied to mine drainage, but it is difficult to constantly meet environmental standards for the final effluent of Mn concentration and pH due to variations in stream flow rate, as non-contamination stream water reacts with steelmaking slag and produces alkaline water, which then reacts with mine drainage to remove Mn. But this study treated Mn and Ni, which are difficult to remove by passive treatment, using a slag reactor. The primary reaction material used in this study, steelmaking slag, can replace $Ca(OH)_2$, the most commonly used neutralizing agent for mine drainage, as an alkaline agent. It also has the advantage of reducing CO_2 emissions from $Ca(OH)_2$ manufacturing processes and recycling waste generated from steel mills.

Materials and methods

Steelmaking slag and limestone

The steelmaking slag used in the experiment had a 2–5mm particle diameter and was composed of Fe oxides, CaO, SiO_2, MnO, MgO, P_2O_5, and TiO_2. Based on previous research, the limestone with a 3–5cm particle diameter was mixed with the slag at a

volumetric ratio of 4:6. Both materials were washed with distilled water before use.

Bench-scale slag reactor

The bench-scale slag reactor, with a volume of 491 mL and a 4:6 volume ratio of steelmaking slag and limestone, was used to treat Mn and Ni reagents dissolved in mine drainage from Taewoo coal mine in Cheong Ju, South Korea, for 456 days. The reactor used a downflow from the upper inlet with a pore volume of 173 mL and a porosity of 38%. And manganese, nickel, and iron sulfate reagents modified the mine drainage composition.

Pilot-scale slag reactor

The study assessed three types of slag reactors for their efficiency in removing manganese from Cheongsan coal mine water in Boeun, South Korea. The characteristics of mine drainage quality in the Cheongsan coal mines were that iron was oxidized and existed as suspended solids before reaching the surface, which could cause clogging in the reactors. Therefore, an upper baffle-type precipitation tank was assessed as a pretreatment process to minimize this phenomenon. This study also estimated the hydraulic conductivity in the slag reactor using Darcy's law to derive process and design factors for a full-scale passive treatment facility.

Results and discussion

Results of bench-scale slag reactor

In the initial stabilization stage, the pH rose to 9 due to active elution of CaO, resulting in Mn of 0.3-0.57 mg/L, Ni 0.07-0.37 mg/L, and Fe concentration was 0.0-0.41 mg/L if simulating the case when untreated Fe was inflowed to before the slag reactor. Fe was inflowed only in the initial stabilizing stage. As a result, manganese was mostly saturated with manganite and hausmannite. In the Acidic (1st) stage, when acidic influent with Mn 2.9-6.9 mg/L inflows, Mn is removed to 2 mg/L at a residence time of more than 12 hours. In the Acidic (2nd) stage, the removal efficiency of Ni increases as the residence time required for treatment increases, and a pH of 7.4 or higher is required. The residence time to remove Ni at 2.7-4.5 mg/L is more than 20 hours when the influent pH is acidic. Manganese removal efficiency improved with longer residence time for neutral influent with a pH of 6.96-8.16, except for some samples taken at short residence times. Manganese concentrations were 0-1.1 mg/L at around 2 hours of residence time. In the Neutral (2nd-1) phase, a relatively short residence time of 0.5-2.0 hours, they have achieved Mn concentrations ranging from 0.1-0.5 mg/L. Manganese was mostly saturated with manganite in this case. A neutral influent with
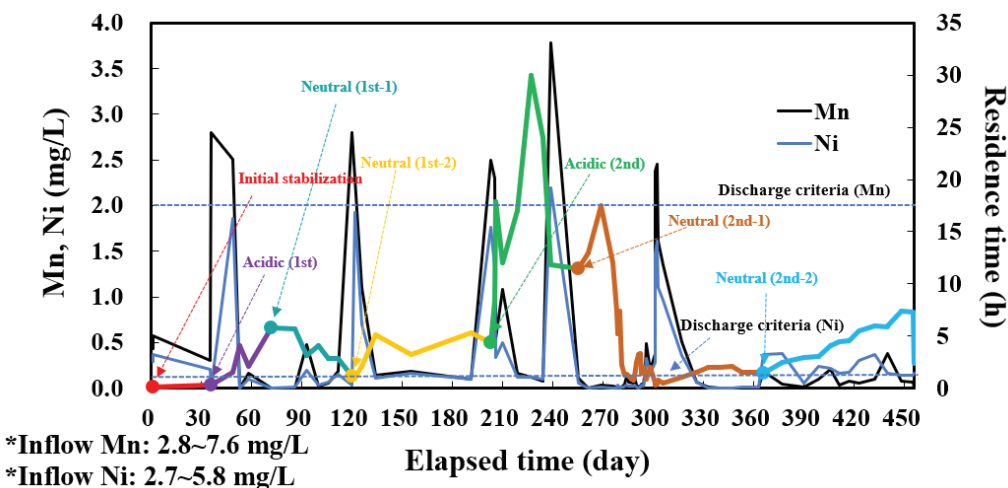

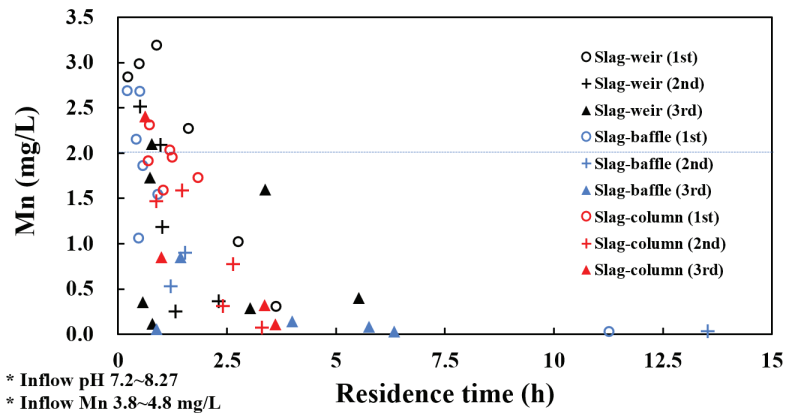*Figure 1* Results of bench-scale slag reactor with 7 phases

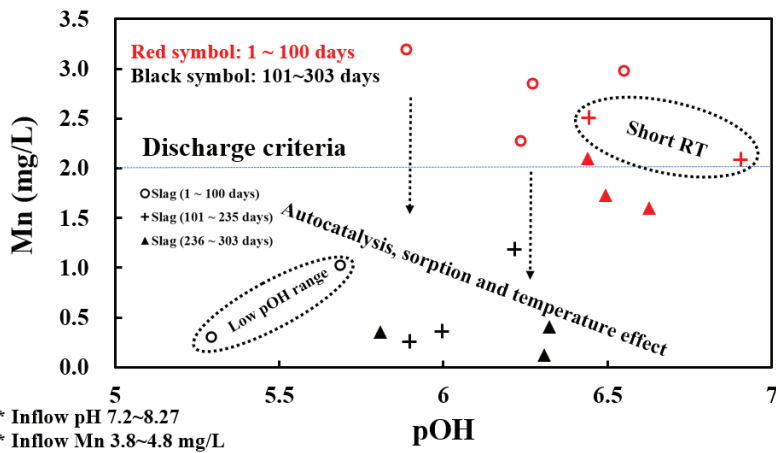*Figure 2 Results according to an operating period of three types of pilot-scale slag reactors*

Figure 3 Mn concentration according to the pOH of the weir-type slag reactor

Ni concentrations of 2.76-5.46 mg/L and pH 7.03-7.89 was inflowed. Ni removal efficiency improved with longer residence time due to residual hydrogen ions from the acidic inflow. Ni removal efficiency was similar to Mn removal efficiency and was affected by acidic influent washing and deionized water effect. In the Neutral (2nd-1) phase, Ni was mostly removed at concentrations of 0.002-0.020 mg/L over a residence time of 1.0-3.5 hours. The results of the PHREEQC geochemical model showed that Ni was generally undersaturated with $Ni(OH)_2$ and $NiCO_3$. SEM-EDS analysis of the black precipitate inside the column showed flower-like crystal structures similar to birnessite.

Results of pilot-scale slag reactor

The efficiency of Mn removal was assessed for three types of reactors (weir, baffle, column) installed in the Cheongsan coal mine in Boeun, South Korea. The Baffle-type slag reactor had the highest removal efficiency, followed by the Column and Weir-type slag reactors. The Column-type slag reactor showed higher Mn removal efficiency as the residence time increased. The Weir-type slag reactor showed a similar trend to the Baffle and Column types for a residence time of 1.5–3.5 hours. The pilot experiment results showed saturation with calcite, manganite, and rhodochrosite, attributed to the influent's high Ca concentration and alkalinity and

the release of CaO and $CaCO_3$ from the slag reactor.

Mn removal efficiency increased as the slag reactor's operation period progressed, and the residence time became longer. It is estimated that the high Mn removal efficiency was due to Mn autocatalytic oxidation and adsorption by accumulated manganese precipitates in the slag reactor. MnO_2, the final oxidized form of Mn, is known to be effectively removed by autocatalytic oxidation of Mn. The Mn removal efficiency increased in a similar pOH range over time, and it increased due to the seasonal effect of increasing water temperature (Fig 3). These results were observed in the other types of slag reactors.

Conclusion

This study investigated the removal of manganese (Mn) and nickel (Ni) from mine drainage using slag reactors under different pH conditions and residence times. The results showed that the removal efficiency of Mn and Ni was influenced by the residence time and pH level. The pilot experiments showed that the baffle-type slag reactor had the highest removal efficiency. This study also derived process design factors for the passive treatment facilities of the Cheongsan and Taewoo coal mines in South Korea, which included using slag reactors with a mechanism for precipitating manganese hydro (oxide)s series and other carbonates form. This study suggests that the autocatalytic oxidation and adsorption effect of the accumulated manganese precipitate could positively affect Mn and Ni removal efficiency.

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