Assessing Removal Efficiencies of Mn and Ni in Mine Drainage Using a Bench-scale Slag Reactor

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Abstract

Mine drainage containing Mn and Ni was treated using a bench-scale slag reactor packed with steelmaking slag and limestone. The reactor was operated for 456 days across seven stages under alternating acidic and neutral inflow conditions. Under neutral conditions with residence times exceeding 3 h, removal efficiencies of both Mn and Ni exceeded 90%. PHREEQC geochemical modeling indicated that the effluent was saturated with respect to Mn (hydr)oxide minerals, while $Ni(OH)_2$ remained unsaturated. SEM–EDS analysis of precipitates revealed flower-like Mn (hydr)oxide aggregates containing Ni (9.5 at.%), providing direct evidence of Ni removal via Mn (hydr)oxide-mediated adsorption rather than direct precipitation.

Keywords: Coal mining, irrigation, green hydrogen, coal-fired power, water reuse

Introduction

Manganese (Mn) and nickel (Ni) are persistent contaminants in coal mine drainage and remain among the most challenging metals to remove by passive treatment. Conventional Mn removal requires chemical oxidation at pH > 9 using $Ca(OH)_2$ or NaOH, entailing substantial operational costs and CO_2 emissions from lime production. Ni removal is similarly difficult because direct precipitation of $Ni(OH)_2$ requires pH values above approximately 8.5–9.0, conditions that are difficult to maintain in passive systems.

Steelmaking slag has been investigated as a reactive medium for passive mine drainage treatment owing to its high alkalinity-generating capacity. In a preceding pilot-scale study, Im *et al.* (2026) assessed three slag reactor configurations (baffle-type, weir-type, vertical flow-type) using steelmaking slag mixed with limestone (4:6 v/v) for Mn removal from coal mine drainage over 316 days. All reactors reduced Mn below the South Korean effluent standard (2 mg L^{-1}) within residence times of approximately 1–2 h; XPS and SEM–EDS analysis confirmed that accumulated precipitates were predominantly Mn(III,IV) (hydr)oxides structurally similar to birnessite; and the progressive improvement in removal efficiency was attributed to autocatalytic oxidation by accumulated Mn (hydr)oxides. However, that study focused exclusively on Mn and did not investigate the co-removal of other dissolved metals.

Birnessite (δ-MnO_2) has a low point of zero charge (PZC ≈ 2.0–2.5) and carries a strong negative surface charge under circum-neutral to alkaline conditions, rendering it an effective sorbent for divalent cations such as Ni^{2+}. If birnessite forms as a secondary precipitate within slag reactors during Mn removal, it may simultaneously enable

Ni removal through surface adsorption, achieving coupled multi-metal treatment in a single process.

The objectives of the present study were to: (1) evaluate the long-term Mn and Ni removal performance of a bench-scale slag reactor over 456 days under alternating acidic and neutral inflow conditions; (2) identify the dominant Ni removal mechanism through PHREEQC geochemical modeling and SEM–EDS characterization; and (3) assess whether the Mn (hydr)oxide precipitates also function as sorbents for dissolved Ni.

Materials and Methods

The reactive media consisted of steelmaking slag (a by-product of iron and steel production with high alkalinity-generating capacity, particle diameter 2–5 mm) and limestone (3–5 cm), mixed at a volumetric ratio of 4:6. The slag was composed of Fe oxides (40.9%), CaO (36.5%), SiO_2 (9.59%), MnO (4.07%), MgO (3.51%), P_2O_5 (1.52%), and TiO_2 (0.89%) based on XRF analysis. The media composition, mixing ratio, and analytical methods followed those described in Im *et al.* (2026). Both materials were washed with distilled water before use.

The bench-scale slag reactor was used to treat mine drainage from the Taewoo coal mine in Cheongju, South Korea, for 456 days. The reactor used a downflow configuration with a porosity of 38%. Mn and Ni sulfate reagents were added to modify the mine drainage composition. Inflow Mn concentrations ranged from 0.4 to 7.7 mg L^{-1} and Ni from 1.4 to 5.8 mg L^{-1} (excluding the initial stabilization stage). Inflow pH was artificially modified through laboratory acidification of the field-collected mine drainage to simulate the seasonal acidity fluctuations commonly observed in coal mine drainages. Operational stages were defined primarily based on changes in inflow pH, while residence time was intentionally adjusted within each stage to evaluate its influence on Mn and Ni removal efficiency. A total of 74 effluent samples were collected across seven operational stages (Table 1).

Effluent temperature, pH, and oxidation–reduction potential (ORP) were measured on-site. Alkalinity was determined by titration with 0.02 N H_2SO_4. Dissolved Ca, Mn, and Ni concentrations were measured by ICP-AES after filtration (0.45 µm) and acidification. Cl^- and SO_4^{2-} were determined by ion chromatography.

Saturation indices (SI) for 11 mineral phases were calculated using PHREEQC version 3.8.6 with the wateq4f.dat thermodynamic database. This database was selected because it includes thermodynamic data for Mn(III,IV) (hydr)oxide and Ni mineral phases.

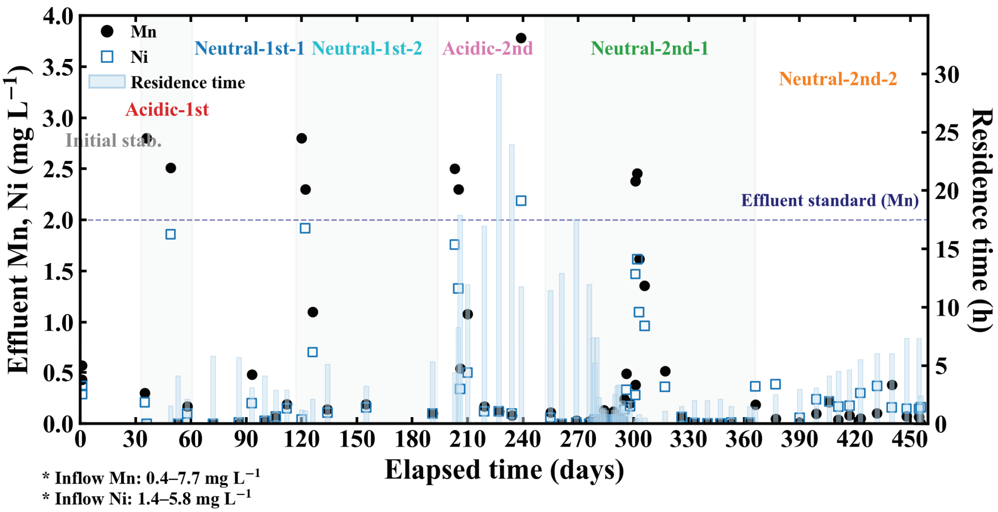
Upon completion of the 456-day operation, precipitate samples were collected from the reactive media surface. SEM–EDS analysis was performed at an accelerating voltage of 15 kV to characterize the morphology and elemental composition of precipitates.

Results and Discussion

Figure 1 shows the temporal variation of effluent Mn and Ni concentrations along with residence time over the 456-day operation. In the initial stabilization stage (days 1–35), the

Table 1 Summary of operational stages for the bench-scale slag reactor. DW = deionized water.

Stage	Designation	Period (days)	Inflow condition	n	RT range (h)
1	Initial stabilization	1–35	Neutral	3	0.10–0.32
2	Acidic-1st	36–58	Acidic (pH 4.5–7.8)	4	0.33–4.10
3	Neutral-1st-1	72–112	Neutral (pH 6.9–7.8)	6	2.90–5.80
4	Neutral-1st-2	120–191	Neutral (pH 7.1–7.6)	6	1.10–5.30
5	Acidic-2nd	203–239	Acidic (pH 4.0–8.1)	8	4.40–30.0
6	Neutral-2nd-1	255–363	Neutral (DW spiking)	34	0.28–17.5
7	Neutral-2nd-2	366–456	Neutral (mine drainage)	13	1.46–7.39



* Inflow Mn: 0.4–7.7 mg L^{-1}
* Inflow Ni: 1.4–5.8 mg L^{-1}

Figure 1 *Temporal variation of effluent Mn and Ni concentrations with residence time across seven operational stages. Dashed line indicates the effluent standard for Mn (2 mg L^{-1}).*

effluent pH remained around 9, consistent with active dissolution of CaO from the slag, resulting in effluent Mn of 0.30–0.57 mg L^{-1} and Ni of 0.21–0.37 mg L^{-1}.

During the Acidic-1st stage, Mn concentration was reduced to <2 mg L^{-1} only at residence times exceeding approximately 2 h, whereas under neutral conditions (Neutral-1st-1), effluent Mn decreased to 0–0.48 mg L^{-1} at residence times of 2.9–5.8 h, comparable to the 1–2 h reported for the pilot-scale reactors (Im *et al.* 2026).

A notable finding not addressed in previous work is the Ni removal behavior. The Acidic-2nd stage demonstrated that Ni removal from inflow concentrations of 3.7–4.5 mg L^{-1} required residence times of >20 h under acidic conditions. Effective Ni removal was observed at effluent pH values as low as ≈7, well below the theoretical pH required for $Ni(OH)_2$ precipitation (≈8.5–9.0), suggesting an adsorption-dominated mechanism rather than direct hydroxide precipitation.

In the later neutral stages (Neutral-2nd-1), the reactor achieved effluent Mn concentrations below 0.2 mg L^{-1} and Ni concentrations of 0.06 mg L^{-1} or below at residence times exceeding 2 h. The progressive improvement in removal efficiency over time is consistent with the autocatalytic effect of accumulated Mn(III,IV) (hydr)oxide precipitates enhancing subsequent metal removal.

Across the neutral-inflow stages, removal efficiency exhibited a sharp threshold around a residence time of 1 h: below this value, median Mn removal was 71% (n = 7), whereas at residence times ≥ 1 h removal plateaued at 98–99% across all longer intervals up to 17.5 h (n = 51). Effluent pH was moderately correlated with both Mn (r = 0.42) and Ni (r = 0.37) removal in the neutral stages. Notably, across all 73 samples, the inflow Mn:Ni molar ratio was strongly anti-correlated with Ni removal efficiency (r = –0.68), consistent with a coupled removal mechanism in which Mn (hydr)oxide accumulation provides sorption sites for Ni^{2+}; when the Mn supply is limited relative to Ni, the Ni removal efficiency declines accordingly.

PHREEQC geochemical modeling revealed that the effluent was frequently saturated (SI > 0) with respect to manganite (MnOOH) under neutral conditions (Figure 2), particularly in the Neutral-1st-1 stage. Calcite and rhodochrosite ($MnCO_3$) also showed SI values near or above zero, suggesting the possibility of concurrent carbonate precipitation.

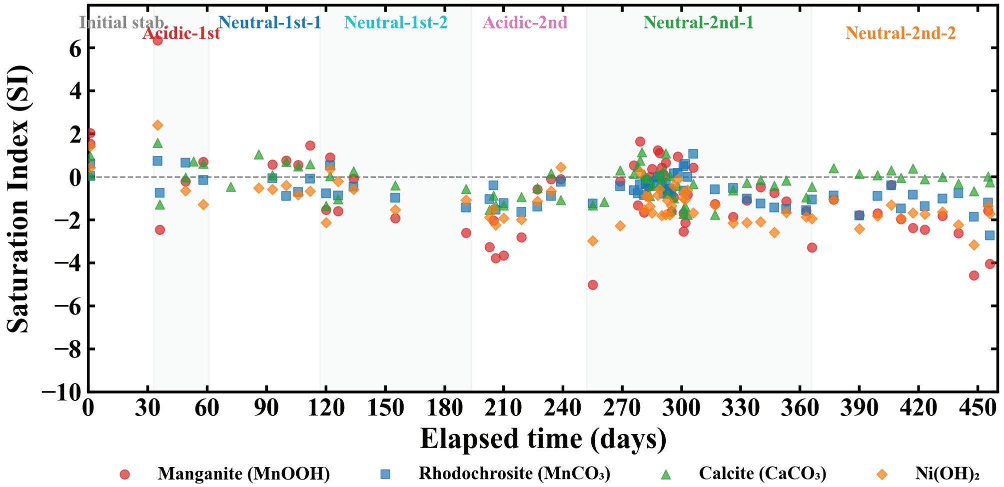


Figure 2 Saturation indices of key Mn and Ni minerals versus elapsed time. Dashed line at SI = 0 indicates equilibrium.

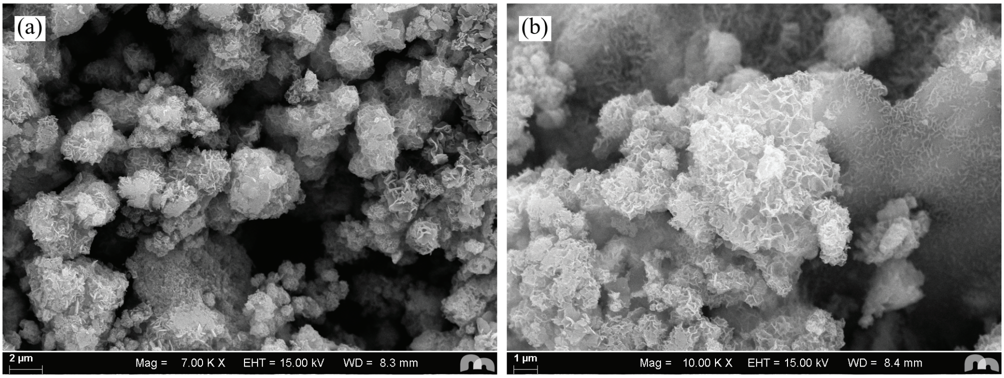


Figure 3 SEM images of precipitates: (a) fine spherical particle aggregates (×7,000); (b) flower-like crystal structures of Mn(III,IV) (hydr)oxides (×10,000).

In contrast, the SI for $Ni(OH)_2$ remained predominantly negative (SI < 0) throughout the experiment, and $NiCO_3$ was unsaturated in most samples. These results indicate that Ni removal cannot be attributed to direct precipitation of Ni hydroxide or carbonate minerals, and an alternative removal pathway, most likely adsorption onto Mn (hydr)oxide surfaces, is suggested.

A notable observation arose during the Neutral-2nd-2 stage (days 366–456), when the median saturation indices of all Mn and Ni mineral phases were negative (manganite −1.96, rhodochrosite −1.05, birnessite −5.60, $Ni(OH)_2$ −1.74) while calcite remained near saturation (SI ≈ 0). Despite this thermodynamic undersaturation, the median effluent Mn and Ni concentrations remained low (0.07 and 0.17 mg L^{-1}, corresponding to ≈98% and 95% removal). This suggests that, by the later operational stages, removal was sustained primarily through adsorption onto the Mn (hydr)oxide surfaces that had progressively accumulated during preceding stages, rather than through new bulk precipitation. The low effluent pH (median 7.5) and reduced alkalinity (mean 0.60 meq L^{-1}) in this stage were thermodynamically unfavorable for further Mn oxide precipitation; however, the low point of zero charge of pre-formed birnessite (PZC ≈ 2.0–2.5) preserved the surface reactivity required for continued Mn^{2+} and Ni^{2+} uptake at circumneutral pH.

SEM imaging of the black precipitates revealed fine spherical particle aggregates with flower-like crystal structures (Figure 3). This morphology was characteristic of Mn(III,IV) (hydr)oxides, consistent with manganite saturation indicated by PHREEQC modeling.

EDS analysis (Table 2) confirmed that the precipitates were dominated by O (53.1 at.%) and Mn (16.3 at.%). Notably, Ni (9.5 at.%) was detected within the Mn (hydr) oxide precipitates, despite $Ni(OH)_2$ being unsaturated in the effluent. This provides direct evidence that Ni accumulated on the Mn (hydr)oxide surfaces through adsorption rather than direct precipitation. While the pilot-scale study did not assess Ni co-removal because only Mn was present in the influent, the present study extends those findings by demonstrating that Mn (hydr) oxide precipitates formed in slag reactors also function as effective sorbents for dissolved Ni.

Based on the combined evidence, the following removal mechanism is proposed. Slag dissolution raises effluent pH, promoting Mn(II) oxidation and precipitation as Mn(III,IV) (hydr)oxide phases, primarily manganite (MnOOH). The accumulated Mn (hydr)oxide precipitates then serve as autocatalytic surfaces that accelerate subsequent Mn(II) oxidation and simultaneously provide adsorption sites for dissolved Ni^{2+}, likely through surface complexation. This coupled mechanism, whereby Mn autocatalytic oxidation is followed by Ni adsorption onto Mn (hydr) oxide surfaces, explains both the progressive improvement in removal efficiency and the effective Ni removal despite $Ni(OH)_2$ remaining thermodynamically unsaturated.

Compared with other passive treatment systems for Mn-contaminated mine drainage, the slag reactor evaluated here achieved Mn removal at residence times (1–2 h) considerably shorter than those typically required for slag leach beds (SLBs) or successive alkalinity-producing systems (SAPS), in which performance is constrained by stream flow variability or limited oxidizing conditions (Im *et al.* 2026). The dual functionality demonstrated here, namely concurrent Mn oxidation and Ni adsorption onto in-situ-formed birnessite-type Mn (hydr)oxides, distinguishes the present slag reactor from earlier slag reactors that targeted Mn removal only via autocatalytic oxidation (Im *et al.* 2026) and from biological systems that rely on sulfate reduction for Ni removal. Achieving multi-metal removal without chemical reagents in a single passive unit positions the slag reactor as a competitive option among existing passive technologies, particularly for coal mine drainages containing both Mn and Ni.

***Table 1** EDS elemental analysis of Mn (hydr)oxide precipitates from the slag reactor (15 kV, × 6,190). Only selected elements are listed.*

Element	Atom %
O	53.06
Mn	16.26
Ni	9.52
C	7.55
Si	3.33
Mg	1.26
Al	0.67
S	0.31

Conclusions

This study demonstrated that a bench-scale slag reactor effectively removed both Mn and Ni from mine drainage over 456 days of continuous operation. Under neutral conditions with residence times exceeding 3 h, removal of both Mn and Ni exceeded 90%. PHREEQC modeling confirmed that the effluent was saturated with respect to manganite while $Ni(OH)_2$ remained unsaturated, and SEM–EDS analysis revealed the presence of Ni (9.5 at.%) within birnessite-type Mn (hydr)oxide precipitates. These results demonstrate that the Mn (hydr)oxides formed in slag reactors contribute not only to autocatalytic Mn oxidation but also serve as effective sorbents for dissolved Ni, enabling coupled multi-metal treatment in a single passive process.

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