A Comprehensive Approach to Fluoride Treatment in Mine Drainage: Chemical Precipitation and Adsorption

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Abstract

Fluoride in mine drainage poses substantial environmental risks, often exceeding South Korea's regulatory discharge limit of 3.0 mg/L. This study assessed treatment processes combining precipitation and adsorption for fluoride and toxic metals from the Samwon mine drainage. To treat aluminum, manganese, and fluoride, experiments involving injection of calcium hydroxide and reaction with slag-limestone mixture were conducted. Subsequently, to treat remnant fluoride, experiments involving precipitation/adsorption using aluminum sulfate and lanthanum chloride as well as adsorption using Al-rich coal mine drainage sludge and domestic water purification sludge were conducted. The results demonstrated substantial fluoride reduction, with adsorption kinetics following a pseudo-second-order model.

Keywords: Fluoride removal, adsorption, precipitation, coprecipitation, aluminum sludge

Introduction

Fluoride and toxic metals in mine drainage present persistent environmental challenges due to their toxicity and potential long-term effects on ecosystems and human health (Hamamoto *et al.*, 2015; Tang *et al.*, 2009). The World Health Organization (WHO, 2017) recommends a fluoride concentration of less than 1.5 mg/L in drinking water, but some mine drainages can exceed this threshold. In addition to fluoride, metals such as manganese, iron, and aluminum are commonly found in elevated concentrations in mine drainage, contributing to water quality deterioration. At the Samwon mine, located in South Korea, mine drainage contains high levels of fluoride (up to 20.5 mg/L), as well as manganese and iron concentrations that exceed national discharge limits. Although aluminum does not have a defined discharge standard, it was included as a treatment target due to its potential to cause environmental issues such as whitening. The geology of the Samwon area consists of Cretaceous granitic rocks and metamorphosed sedimentary rocks, both of which are known sources of fluoride. Fluoride occurs in granitic rocks primarily in Si–F bonds, and its mobility depends on surrounding geochemical conditions, including pH, redox potential, and the presence of competing ions. Once released into groundwater, fluoride may exist as soluble species or precipitate as fluorite (CaF_2).

To address these challenges, this study assessed and compared the performance of different treatment approaches for fluoride and metal removal. In the primary treatment, two separate processes were tested and compared: (1) active precipitation using calcium hydroxide ($Ca(OH)_2$), and (2) passive precipitation using a slag-limestone mixture. These processes were assessed based on their ability to remove aluminum, manganese, iron, and fluoride. In the secondary treatment, two different fluoride removal methods were applied to the water that remained after each primary treatment: (1) chemical precipitation and/or adsorption induced by the addition of aluminum sulfate ($Al_2(SO_4)_3$) or lanthanum chloride ($LaCl_3$), and (2) adsorption using aluminum sludge-based adsorbents from an Al-rich coal mine drainage treatment facility and from a domestic water purification facility (Fig. 1). This study aims to assess and compare each treatment step – both primary and secondary – by examining removal efficiency, economic feasibility, and potential for practical application in mine drainage treatment.

Methods

Adit drainage used in this study was collected from the Samwon mine, South Korea. The water exhibited a near-neutral to slightly acidic pH (average: 6.2) and high electrical conductivity (EC), with elevated concentrations of fluoride (up to 20.5 mg/L), manganese, iron, and aluminum (Tab. 1).

Temperature, oxidation-reduction potential (ORP), pH, EC, and dissolved oxygen (DO) concentrations were measured using an HQ40D multi-portable meter (Hach). Alkalinity was measured using a digital titrator (Hach), and fluoride was analyzed with a DR-900 colorimeter (Hach). Major cations and anions were analyzed by ICP-OES (Varian 720-ES) and ion chromatography (Metrohm 850), respectively.

In the primary treatment stage, two separate processes were assessed and compared. The first method involved active treatment by adding calcium hydroxide ($Ca(OH)_2$) in batch experiments to increase the pH and induce the precipitation of metals and fluoride. The second method applied passive treatment using a slag-limestone mixture at a volumetric ratio of 4:6 in a lab-scale column setup, where hydraulic retention times (HRTs) ranged from 2 to 12 hours. The slag was basic oxygen furnace (BOF) steelmaking slag generated in South Korea. Geochemical modeling using PHREEQC was performed to predict the saturation indices of potential precipitates including gibbsite (Al(OH)3), goethite (FeOOH), magnetite (Fe_3O_4), and fluorite (CaF_2), to understand the dominant removal mechanisms.

Following the primary treatments, two different approaches were tested for secondary fluoride removal. The first method involved chemical dosing using aluminum sulfate ($Al_2(SO_4)_3$) or lanthanum chloride ($LaCl_3$) in batch experiments, which induce

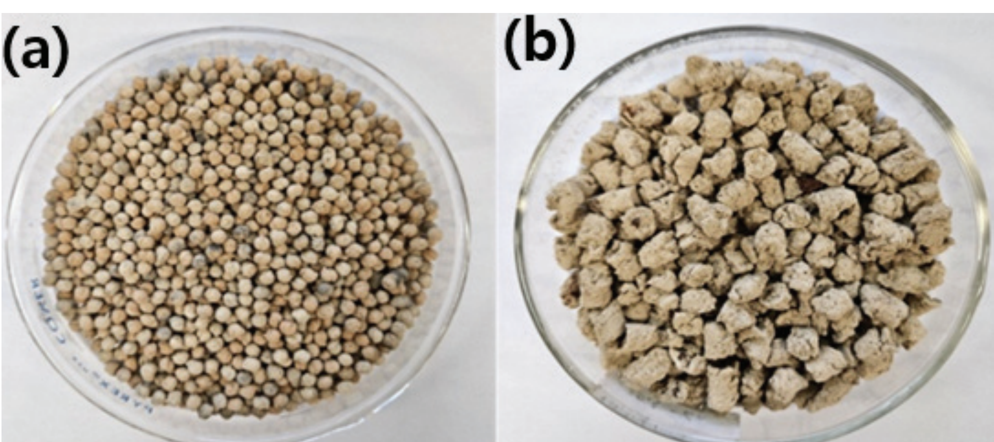

Figure 1 Photographs of the adsorbents used in the secondary treatment process: (a) adsorbent made from sludge of a domestic water purification facility and (b) from sludge of a coal mine drainage treatment facility.

Table 1 Physicochemical characteristics and ion composition of mine drainage collected from the Samwon mine.

Average physicochemical characteristics of mine drainage						Flow rate (m^3/day)	
T (°C)	pH	EC (µS/cm)	DO (mg/L)	Alkalinity (mN)	SS (mg/L)	Avg.	Max.
18.4	6.2	1028.2	6.7	0.87	4.0	129.6	1065.7
Ion concentration (mg/L)							
Fe	Mn	Al	Ni	Cu	Zn	F^-	SO_4^{2-}
4.07	10.75	12.52	0.07	0.01	0.38	35.93	523.80

precipitation and/or adsorption. Dosages were varied to evaluate fluoride removal efficiency and sludge generation. The second method employed two aluminum-based adsorbents: ST, derived from sludge of Samtan (ST) mine drainage treatment facility, and DENS-10, obtained from alum sludge in a domestic water purification facility. Adsorbents were characterized via Brunauer-Emmett-Teller (BET) surface area analysis, Barrett-Joyner-Halenda (BJH) pore distribution, and scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM-EDS). Batch adsorption experiments were conducted under varying pH and solid-to-liquid (S/L) ratios, and adsorption behaviors were assessed using pseudo-first-order and pseudo-second-order kinetic models as well as Langmuir and Freundlich isotherm models.

Results and discussion

Primary treatment using calcium hydroxide effectively increased the pH of mine drainage and facilitated the removal of aluminum, manganese, iron, and fluoride through precipitation. As the pH rose to approximately 10.5, aluminum precipitated as hydroxides, which was supported by PHREEQC modeling. Iron, initially present at 5.8 mg/L, was completely removed at pH above 8.0, likely due to the formation of iron (oxy)hydroxides. While manganese concentrations exceeded 2 mg/L at pH 9.5, they decreased below 0.15 mg/L at pH 10.5, meeting regulatory discharge limits. Fluoride concentration decreased from 20.5 mg/L to 13.7 mg/L after calcium hydroxide addition, and PHREEQC results indicated possible fluorite (CaF2) formation as a key removal mechanism. Although the fluoride concentration decreased after primary treatment, it still exceeded both the WHO guideline of 1.5 mg/L and South Korea's regulatory discharge limit of 3.0 mg/L for high-quality water bodies, indicating the necessity of a secondary treatment process. This study was conducted in accordance with South Korea's regulatory standards for wastewater discharge, and the treatment performance was evaluated based on the national discharge limit of 3.0 mg/L for fluoride.

In the passive treatment using a slag-limestone mixture, the removal of aluminum and manganese was effective at hydraulic retention time (HRT) of ≥4 hours in the column, but fluoride concentrations remained between 13.0 and 17.1 mg/L, again indicating the need for additional treatment.

For chemical-based secondary treatment, the addition of 1,200 mg/L of aluminum sulfate ($Al_2(SO_4)_3$) reduced the fluoride concentration from 13.7 mg/L to 2.8 mg/L within 30 minutes, but produced a large volume of aluminum hydroxide sludge. In contrast, lanthanum chloride ($LaCl_3$) at 400 µL/L achieved similar fluoride removal below 3.0 mg/L with substantially less sludge production. While both reagents were effective, lanthanum chloride showed an advantage in sludge management.

In the adsorption-based secondary treatment, ST and DENS-10 adsorbents were applied to batch experiments. ST showed a higher surface area (168.94 m^2/g) and pore volume (0.53 cm^3/g) than DENS-10 (39.96 m^2/g, 0.14 cm^3/g) (Table 2). Kinetic analysis revealed that both materials followed pseudo-second-order (PSO) kinetics, suggesting chemisorption as the dominant mechanism. ST showed rapid initial uptake but reached saturation earlier, while DENS-10 exhibited more stable adsorption over time. Adsorption

Table 2 BET and BJH analytical results for the DENS-10 and ST adsorbents.

Adsorbent	BET (m^2/g)	Total pore volume (cm^3/g)	dp, peak (nm)	Avg. pore size (nm)	Reference
DENS-10	40	0.14	18.5	14.8	This study
ST	169	0.53	43.6	13.7	This study
$GASA_{(100\ mesh)}$ [1)]	177	0.73	<180.0	–	(Cho et al., 2020)
ASBA[2)]	87	0.11	–	3.6	(Lee et al., 2020)
Activated alumina	357	0.44	–	46.4	(Kim et al., 2005)

1) A granular composite adsorbent prepared from PAC and starch gel

2) Alum-sludge based adsorbent

isotherm results indicated DENS-10 followed Langmuir isotherm implying uniform monolayer adsorption, with a maximum adsorption capacity (qmax) of 12.3 mg/g. In contrast, ST exhibited combined mechanisms involving both surface adsorption and mineral precipitation, supported by SEM observations of fluorite formation on its surface. This may be attributed to residual calcium from the hydrated lime treatment in the Samtan treatment facilities, which reacted with fluoride during adsorption.

Conclusions

This study assessed and compared multiple treatment strategies for fluoride and metal removal from the Samwon mine drainage. The primary treatment using calcium hydroxide and a slag-limestone mixture demonstrated effective removal of aluminum, manganese, iron, and partial fluoride reduction through pH adjustment and precipitation. In the secondary stage, both chemical reagent addition ($Al_2(SO_4)_3$ and $LaCl_3$) and adsorption using aluminum-based materials (ST and DENS-10) were tested. Lanthanum chloride achieved similar fluoride removal to aluminum sulfate while generating less sludge, making it advantageous for sludge management. Between the adsorbents, DENS-10 showed q_{max} of 12.3 mg/g, while ST offered a combined mechanism of surface adsorption and mineral precipitation. Overall, this study demonstrated that the proposed treatment approaches are effective and adaptable depending on site-specific conditions. Future work will focus on field-scale validation and long-term stability.

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