

# Geochemical Processes in Iron-Rich Mine Drainages: Enhancing Passive Treatment Systems through Colloid Stability and CO Reduction

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## Abstract

Mine drainage, especially from abandoned sites, poses a substantial environmental challenge. Passive treatment systems are effective but require understanding geochemical processes. This study focuses on two Japanese abandoned mine sites: the Ainai mine (neutral pH, rich in iron) and the acidic Shojin River. Iron (Fe) colloids play a key role in sequestering toxic elements like arsenic (As) and zinc (Zn). In Ainai, Fe colloids were stable, promoting effective treatment, but in the Shojin River, the colloids were unstable. To address this, basalt was added to raise pH and stabilize Fe colloids, enhancing water quality while also contributing to carbon dioxide removal (CDR).

**Keywords:** Mine drainages, Passive treatment, Fe Colloids, Enhanced Rock Weathering (ERW), Carbon dioxide removal (CDR)

## Introduction

Mine drainage, particularly from abandoned sites, poses an environmental threat due to its potential to contaminate water sources with toxic metals (Nordstrom 2011). Understanding the geochemical processes governing mine drainage is critical for developing effective and sustainable remediation strategies. While active treatment methods, such as chemical dosing and mechanical aeration, provide immediate mitigation, they are often expensive and require continuous maintenance (Johnson and Hallberg 2005). In contrast, passive treatment systems harness natural geochemical and biological processes to improve water quality in a more cost-effective and environmentally sustainable manner (Gandy *et al.* 2016).

Although Iron (Fe) colloids can act as transportation vectors for toxic elements, they also play a crucial role in passive treatment, by sequestering toxic elements such as arsenic

(As) and zinc (Zn), thereby reducing their mobility in aquatic systems (Hsu *et al.* 2010). Additionally, the dissolution of silicate rocks, such as basalt, contributes to carbon dioxide (CO<sub>2</sub>) removal through enhanced rock weathering (ERW), a process that facilitates long-term carbon sequestration (Beerling *et al.* 2020). However, the stability and efficiency of Fe colloids are highly dependent on pH conditions, which vary across different mine drainage environments (Younger *et al.* 2002).

A novel aspect of this study is the integration of ERW with acid mine drainage (AMD) remediation, leveraging the concept that the carbon dioxide removal (CDR) efficiency of ERW is directly linked to the mineral dissolution rate in ultramafic rocks (in this case, basalt). Studies on water-rock interactions suggest that mineral dissolution occurs more rapidly in acidic, dynamic systems such as AMD compared to stagnant,

neutral environments like agricultural soils (Renforth *et al.* 2015). Consequently, ERW may achieve higher carbon sequestration efficiency in AMD settings, providing an additional environmental benefit beyond conventional mine drainage treatment.

This study investigates mine drainage at two abandoned sites in Japan (Fig. 1): the Ainai Mine, characterized by neutral pH and Fe-rich conditions, and the acidic Shojin River (Fig. 1). The Ainai mine drainage system utilizes aeration to promote Fe oxidation and precipitation, while the Shojin River employs a limestone bed to neutralize acidity and remove Fe, As, and Zn. Given the acidic nature of the Shojin River, basalt was put into the river to increase pH and consequently, stabilize Fe colloids.

Based on this background, this study aims to (i) characterize the nature of Fe colloids in neutral and acidic mine drainage systems, (ii) assess the sequestration efficiency of Fe colloids for toxic metal removal and (iii) investigate the efficiency of basalt in stabilizing Fe colloids in acidic environments. By integrating ERW with AMD remediation, this approach not only enhances the sequestration of toxic elements but also contributes to CO<sub>2</sub> reduction, demonstrating the additional environmental benefits of passive treatment strategies.

## Methods

Onsite measurements were conducted at the sampling sites, including pH, electrical conductivity (EC), dissolved oxygen (DO), redox potential (ORP), turbidity, alkalinity, and temperature. Alkalinity, expressed as HCO<sub>3</sub><sup>-</sup>, was determined by titrating a 50 mL water sample (filtered through a 0.45 µm filter) with 0.16 N HNO<sub>3</sub>, following the USGS guidelines (Rounds 2012). Dissolved ferrous iron (Fe<sup>2+</sup>) was measured using an ion-selective pack from Kyoritsu Chemical Check Lab., Corp.

Water samples were collected for the analysis of various parameters, including cations, anions, and dissolved colloidal fractions. The collected water was filtered using 0.20-micrometer membrane filters and stored in 50 mL acid-washed polyethylene bottles. Samples for dissolved colloidal fraction analysis underwent additional filtration using nano-membrane filters with a molecular weight cutoff of 200 kDa. To preserve cation samples, 1% (v/v) ultrapure nitric acid was added.

Precipitated sediments from the drainage were collected for mineralogical and chemical characterization. Additionally, ultrafiltration at each sampling point enabled the collection and physical observation of colloids retained on the ultrafilters.

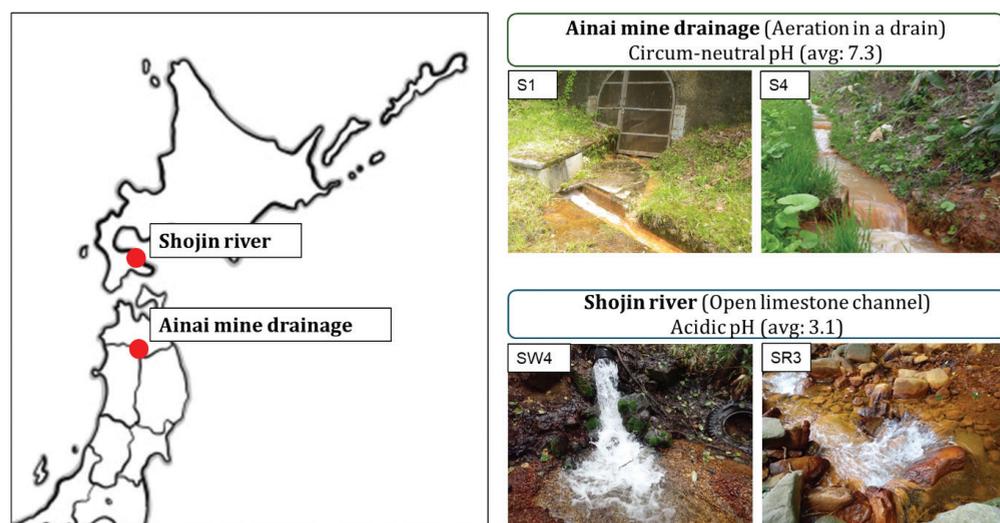


Figure 1 Location of Shojin river and Ainai mine drainage, along with their field pictures.



For the field trial, approximately 1 ton of crushed basalt particles (5 cm in diameter) was introduced into the Shojin River. Water samples were analyzed before and after interaction with the basalt to assess changes in water chemistry. Sampling was conducted over a period of two months to evaluate the long-term effects of basalt addition on pH stabilization, Fe colloid stability, and toxic metal sequestration.

## Results and Discussion

### *Trends of Fe and As in dissolved and colloidal fractions*

#### Ainai Mine Drainage

The onsite measurements at the Ainai Mine indicate a neutral to alkaline system, with pH values ranging from 6.20 to 7.91 (Fig. 2a). Downstream, the pH increases while alkalinity decreases, suggesting carbonate buffering effects. The geochemical analysis indicates that  $\text{Fe}^{2+}$  concentrations decrease downstream, accompanied by increasing turbidity, implying Fe (oxy)hydroxide nanoparticle formation and aggregation. The inverse relationship between turbidity and  $\text{Fe}^{2+}$  concentrations suggests that oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  leads to precipitation and increased turbidity (Hsu *et al.* 2010).

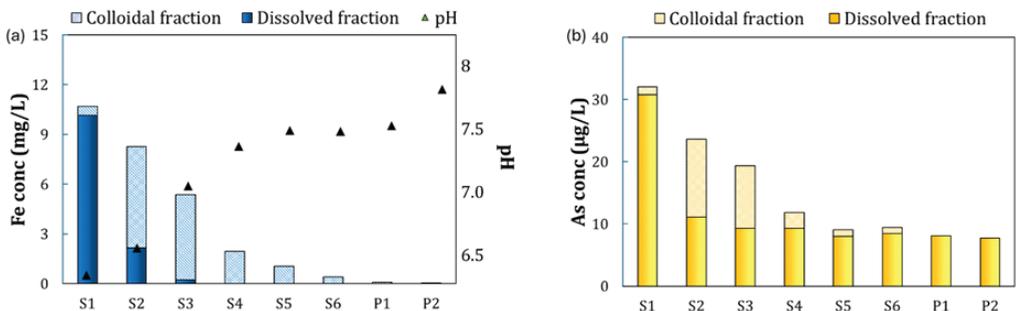
Arsenic (As), primarily present as arsenite [As(III)], follows Fe in its distribution (Fig. 2b). The formation of Fe colloids at sites S2 and S3 suggests that Fe colloids act as primary carriers, while As behaves as a pseudo-colloid, its mobility largely governed by Fe colloids.

The inverse correlation between Fe and As concentrations suggests that As removal occurs through adsorption, co-precipitation, and aggregation with Fe colloids (Gandy *et al.* 2016). However, further downstream, As persists in the dissolved phase, likely due to Fe-Si associations that reduce Fe oxide affinity for As (Younger *et al.* 2002).

#### Shojin River

In contrast, the Shojin River represents an acidic mine drainage system (Fig. 3a). The background site (SR1) has a near-neutral pH (6.9), but wastewater from the abandoned mine is highly acidic (pH: 2.8). The wastewater samples (SW1, SW2, SW4) contain elevated Fe and As concentrations, exceeding WHO limits (Fe: 10 mg/L, As: 10  $\mu\text{g/L}$ ). Upon mixing with uncontaminated river water at SR2, elemental concentrations decrease progressively downstream, reaching levels below WHO limits by SR9.

Colloidal and dissolved fractions, absent in initial wastewater and river water, emerge from SR2 onward. Fe and As exist in both dissolved and colloidal forms but transition predominantly to the dissolved phase from SR6. Element concentrations inversely correlate with pH, decreasing as pH increases. The formation of Fe colloids initially facilitates As sequestration (Fig. 3b); however, in the Shojin River, Fe colloids appear unstable (Fig. 3b, SR3 to SR5) and prone to dissolution, potentially re-releasing As into the water column (Nordstrom 2011).



**Figure 2** Trends of dissolved and colloidal fractions of (a) Fe and (b) As concentrations at Ainai mine drainage. S1 to S6 represent the sampling points at Ainai mine drainage. P1 and P2 are ponds set up at the downstream of the aeration channel before the water flows to a nearby river.

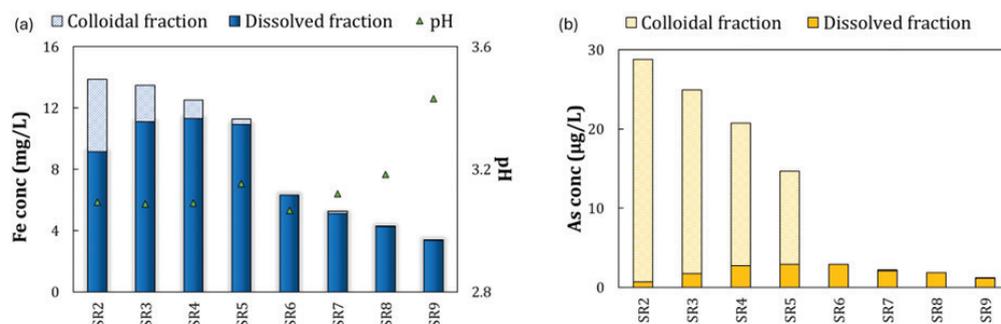


Figure 3 Trends of dissolved and colloidal fractions of (a) Fe and (b) As concentrations at Shojin river. SR represents sampling location from SR2 (mixing point with background river water) and flows towards the downstream at SR9, before emptying into the Japan sea.

### Mineralogy of colloids, sediments, and suspended particles

Microscopic analysis of the colloids collected on the ultrafilters confirmed that mineralogy in the mine drainage is pH-dependent, with schwertmannite forming in acidic conditions and ferrihydrite dominating at neutral to slightly alkaline pH (Fig. 4a and b). At the Shojin River, schwertmannite was identified in both sediments and colloids, exhibiting its characteristic fibrous structure. TEM analysis further revealed schwertmannite as fibrous aggregates with spheroidal hedgehog morphologies, composed of Fe, S, C, O, and minor As, as detected by EDS. These particles measured 50–80 nm on average. The formation of schwertmannite is primarily controlled by  $\text{Fe}^{3+}$  hydrolysis under acidic

conditions (Bigham *et al.* 1996). Solid-phase analyses suggest that schwertmannite plays a crucial role in As scavenging, making it a key component in AMD environments (Regenspurg *et al.* 2004).

In contrast, at the Ainai mine drainage, XRD analysis of sediments and suspended particles identified 2-line ferrihydrite as the dominant Fe hydroxide mineral. Ferrihydrite formation is favored under circumneutral conditions, resulting from  $\text{Fe}^{2+}$  oxidation and subsequent hydrolysis (Cornell and Schwertmann, 2003). EDS analysis confirmed that the colloids in Ainai drainage primarily consist of 2-line ferrihydrite, which exhibits high affinity for toxic element sequestration (Webster *et al.*, 1998). The stability and reactivity of ferrihydrite make it a key

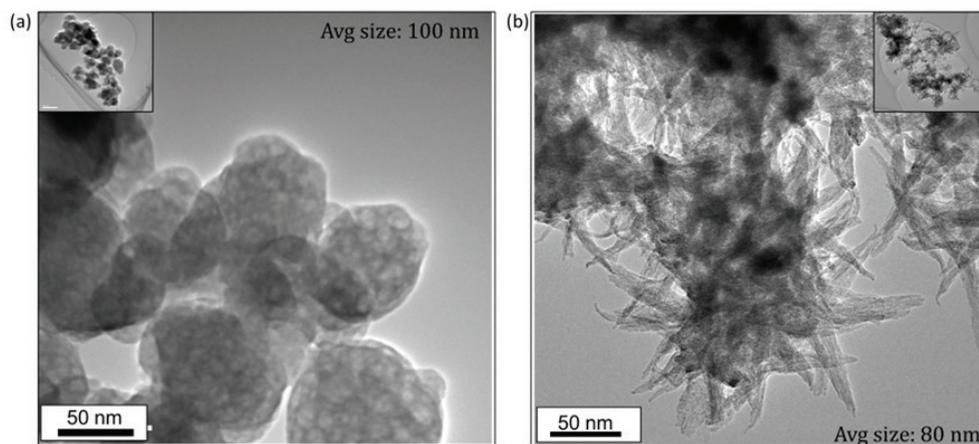


Figure 4 Morphology (a) Core-shell ferrihydrite aggregates at Ainai mine drainage and (b) fibrous schwertmannite colloids at Shojin.



component in passive treatment systems (Legg *et al.*, 2014).

### *Integration of mine drainage treatment with CO<sub>2</sub> reduction*

Schwertmannite colloids formed in the acidic Shojin River system exhibited dissolution behavior, primarily influenced by the low pH of the system. The state of schwertmannite in strongly acidic environments is well-documented, as it tends to dissolve and release previously adsorbed elements, including arsenic (As) (Regenspurg *et al.*, 2004). To improve water quality and enhance colloid stability, basalt was introduced to the system to promote pH buffering (Fig. 5).

On-site measurements revealed a gradual increase in pH following basalt addition, a key factor in stabilizing schwertmannite colloids and enhancing As sequestration. After one month of this flow through-basalt interaction, the pH increased to an average of 3.7 from 3.2, a trend attributed to the dissolution of basaltic minerals, which release alkaline species into the water (Renforth *et al.*, 2015). This increase in pH facilitates the transformation of schwertmannite into more stable Fe hydroxides, thereby reducing

the risk of As remobilization (Bigham *et al.*, 1996).

Continued interaction between acidic mine drainage and basalt results in the dissolution of silicate minerals, contributing bicarbonate ions (HCO<sub>3</sub><sup>-</sup>) to the system. These ions eventually reach downstream environments, where they enhance ocean alkalinity, potentially increasing CO<sub>2</sub> sequestration through enhanced weathering processes (Beerling *et al.*, 2020). This mechanism highlights the dual benefit of basalt addition—not only improving the stability of Fe colloids in AMD systems but also contributing to global carbon cycle regulation.

### **Conclusions**

This study highlights the crucial role of Fe colloids, particularly schwertmannite and ferrihydrite, in the sequestration of toxic elements such as arsenic (As) in mine drainage systems. The findings demonstrate that pH plays a fundamental role in controlling the mineralogy and stability of Fe colloids, with schwertmannite dominating in low-pH environments and ferrihydrite forming under neutral conditions.

Upon installation



1 Month later



**Figure 5** Pictures of increased precipitation at the Shojin river on the surface of basalt bags. (Left) Gray-ish basalt bags along the river and (right) 1 month after basalt application.

In the acidic Shojin River, schwertmannite was found to be unstable, leading to potential As re-release. However, the introduction of basalt improved water quality by increasing pH, thereby enhancing the stability of Fe colloids and promoting As sequestration. The interaction between basalt and acidic drainage facilitated the dissolution of silicate minerals, releasing bicarbonate ions that contribute to ocean alkalinity and CO<sub>2</sub> reduction.

Overall, this study underscores the potential of enhanced rock weathering as a dual-benefit strategy for mine drainage remediation and climate change mitigation. By integrating geochemical processes with passive treatment approaches, this method offers a sustainable solution for managing mine-impacted waters while contributing to long-term carbon sequestration.

## Acknowledgements

The authors thank all Hokkaido Research Organization for their cooperation during the research. We extend our gratitude to all those who contributed to our research, particularly Mr. F Nakamura, Ms. N. Kimotsuki and Mr. Naito for their assistance with our field work and some analysis. This research was supported by a Joint research grant from Research Grant of the “Nanotechnology Platform” Program of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan; New Energy and Industrial Technology Development Organization (NEDO); the Japan Society for the Promotion of Science (JSPS) KAKENHI; and the Japan International Cooperation Agency (JICA). The authors also thank all co-organisers for hosting the IMWA 2025 Conference.

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