Treatment of Simulated Copper-Zinc-Bearing Acid Mine Drainage Using Scrap-Derived Aluminum–Iron Bimetals and Implications For Downstream Metal Recovery

Dayle Tranz Dano[1], Ilhwan Park[1], Mayumi Ito[1], Carlito Tabelin[2], Vannie Joy Resabal[2]

[1]*Division of Sustainable Resources Engineering, Hokkaido University, Sapporo 060-8628, Japan, dayletranz.dano@gmail.com*

[2]*Department of Materials and Resources Engineering and Technology, College of Engineering, Mindanao State University-Iligan Institute of Technology, Iligan City 9200, Philippines*

Abstract

Acid mine drainage (AMD) is widely managed as an environmental liability, yet the same dissolved metals that drive its toxicity make it an untapped secondary resource. This study evaluated Al–Fe bimetallic particles synthesized directly from scrap aluminum filings for the capture of Cu and Zn from simulated AMD. At 20 g/L and 120 min, the bimetal removed essentially all Cu and 98% of Zn while raising pH from 2.12 to 5.7. Surface analyses indicated Cu capture proceeded mainly by electrochemical reduction, whereas Zn involved combined reduction and co-precipitation with in situ Al/Fe oxyhydroxides – establishing groundwork for downstream metal recovery.

Keywords: AMD treatment, metal removal, circular remediation

Introduction

Acid mine drainage (AMD), an acidic and metal-rich effluent generated by mining activities, remains one of the most enduring legacies of the industry. Its consequences are far-reaching, degrading water quality, damaging ecosystems, and posing risks to human health. For this reason, AMD has traditionally been treated primarily as an environmental liability that requires containment, neutralization, and continuous management – a persistent economic burden alongside its environmental cost (Johnson and Hallberg 2005). In recent years, however, a paradigm shift in the approach to AMD is emerging. The same dissolved constituents that make AMD problematic position it as a viable secondary source of valuable metals.

Conventional AMD treatment has been essential for protecting downstream water systems, yet most approaches remain centered on contaminant removal rather than resource recovery. Neutralization and precipitation methods can effectively lower dissolved metal concentrations, but they often rely on continuous reagent input and generate mixed sludge with limited direct commercial value (Fu and Wang 2011). Additionally, AMD is not an easy resource to valorize because metals are present in relatively dilute concentrations within chemically complex aqueous matrices, where acidity, sulfate, and coexisting ions can strongly influence selectivity and reaction pathways (Aghaei *et al.* 2021). This complexity helps explain why many proposed recovery technologies, although promising under controlled laboratory conditions, remain challenging to justify in practice. For mine water applications, a useful recovery method must be more than chemically effective; it must also be sustainable from both environmental and economic perspectives.

In this context, reactive bimetallic materials offer a promising alternative. Bimetals are composite materials composed of two dissimilar metals with different electrochemical behavior, allowing them to exhibit reactivity distinct from that of their individual components. Owing to their strong reductive potential, such materials have been widely explored in wastewater treatment applications (Aghaei *et al.* 2022). Their effectiveness arises from localized

galvanic interactions formed between the coupled metals, in which the more active metal functions as a sacrificial anode and the more noble metal serves as the cathodic site. This galvanic coupling enhances electron transfer, sustains reductive recovery, and can improve contaminant removal efficiency (Xiang *et al.* 2018). In acidic and metal-laden systems such as AMD, these characteristics make bimetals particularly attractive as reactive materials for metal recovery.

In selecting the bimetal composition, Al and Fe are particularly attractive because they are widely available, relatively inexpensive, and electrochemically complementary compared with more noble metals. Individually, both aluminum- and iron-based materials have been applied in wastewater treatment, but their reactivity is often limited by rapid oxide passivation at the surface (Plessl *et al.* 2023). When synthesized as a bimetal, however, this drawback can be partly overcome through galvanic interaction between the two metals. In the Al–Fe system, Al, with its more negative standard reduction potential (Al^{3+}/Al: E^0 = -1.66 V), acts as the sacrificial anode, whereas Fe (Fe^{3+}/Fe: E^0 = -0.04 V) serves as the cathodic partner that facilitates electron transfer and reductive reactions at the surface. As a result, the coupled system exhibits a reactivity distinct from that of either metal alone, making Al–Fe bimetals a promising low-cost candidate for metal recovery applications.

Building on these considerations, this study examines scrap-derived Al–Fe bimetallic particles – synthesized directly from waste aluminum filings – for the capture of Cu and Zn from simulated AMD. This dual-waste framing couples the upcycling of an industrial waste stream with the treatment of a persistent mining effluent, addressing both within a single material system. The effects of contact time and bimetal dosage on metal removal and solution pH are evaluated alongside the surface reactions and resulting metal speciation that govern capture. Together, these results establish the mechanistic basis on which downstream metal recovery from mine-affected waters can be developed in future work.

Methods

Preparation of Simulated Acid Mine Drainage

In this study, synthetic AMD was chemically prepared to replicate the composition of real AMD obtained from an operating copper mine in the Philippines. Table 1 presents the assayed concentrations (mg/L) of individual metals in the real AMD. Preparation of the synthetic AMD involved the use of metal sulfate forms of Ni, Cu, Zn, and Mn, as well as sodium chloride (NaCl), calcium chloride ($CaCl_2$), and sodium sulfate (Na_2SO_4). To achieve the target pH (2.0–2.2) similar to AMD, dilute hydrochloric acid (HCl) was added to the synthetic AMD.

Synthesis of Al–Fe Bimetals using Scrap Aluminum

Al–Fe bimetallic particles were synthesized following a published two-stage mechanical–chemical method using scrap Al (Tabelin *et al.* 2021). Unlike the reference study, shredded aluminum filings from Iligan City, Philippines were used instead of aluminum cuboids, thereby eliminating the need for surface mechanical polishing and likely enhancing reactivity because of the higher surface area. The scrap was sieved, washed with deionized water, and vacuum dried before a pre-weighed sample was placed in an Erlenmeyer flask. An HCl–NaCl–$FeCl_3$ reagent mixture was then added to remove the native oxide/anodized layer and supply Fe^{3+} ions for reduction at the aluminum surface. The reagent mixture consisted of 0.125 M HCl, 0.125 M NaCl, and 1.25 M $FeCl_3$.

Table 1 *Initial solute concentrations (mg/L) in the real AMD.*

Components	Cu	Fe	Mn	Ni	Zn	Al	Mg	Ca	SO_4^{2-}
Concentration (mg/L)	10.4	17.1	6.9	1.5	7.4	27.8	25.8	352.2	1,752.0

Batch Removal Experiments of Cu and Zn from Simulated AMD

The performance of Al–Fe bimetallic materials in removing Cu and Zn from synthetic AMD was investigated through batch removal experiments conducted in triplicate. A predetermined dosage of the bimetallic material (5, 10, and 20 g/L) was placed in an Erlenmeyer flask and mixed with simulated AMD. This suspension was then placed in a thermostat water bath shaker with 40 mm of shaking amplitude and 110 min−1 of shaking frequency at 25 °C for 5–120 min. After the predetermined reaction time, the filtrates were collected, filtered through syringe-driven membrane filters (pore size: 0.2 µm), and analyzed by ICP-AES (ICPE-9820, Shimadzu Corporation, Japan; instrument error ±2%) to quantify the concentrations of Cu and Zn. The removal of target metal ions (%R) was determined in percentage using the equation:

$$\%R = [(C_0 - C) / C_0] \times 100$$

where C_0 is the initial metal concentration in mg/L, and C is the residual metal ion concentration in mg/L. This metric quantifies the loss of dissolved Cu and Zn from the aqueous phase and does not represent the mass of metal recovered as a separable product; downstream recovery is treated here as a future implication informed by the observed surface speciation.

Results

Characterization of Synthesized Al–Fe Bimetal from Scrap Al

Scrap Al and the synthesized bimetal were characterized using XRF, SEM-EDS, and XPS. Scrap Al was mainly Al (>95%) with minor Si, Fe, and Mg typical of Al alloys. After synthesis, Fe content increased from 0.6% to 40.4% (Figure 1), and XPS confirmed zero-valent Fe (ZVI) deposited on the Al surface.

Copper and Zinc Removal from Synthetic Acid Mine Drainage and pH Changes

Figure 2 shows that the Al–Fe bimetal removed both Cu and Zn from simulated AMD under all tested conditions, with removal rates improving at longer times and higher dosages. Cu was removed faster and more completely, reaching full removal within 20 min at 20 g/L, while Zn required 120 min at the same dosage to approach 98% removal – indicating Cu is more readily removed than Zn.

This difference reflects electrochemical favorability: Cu, the more noble metal, has a larger electrode-potential difference relative to Al than Zn, making its reduction thermodynamically more favorable. Longer treatment times and higher dosages increased exposure and reactive-site availability, driving progressively higher removals for both metals.

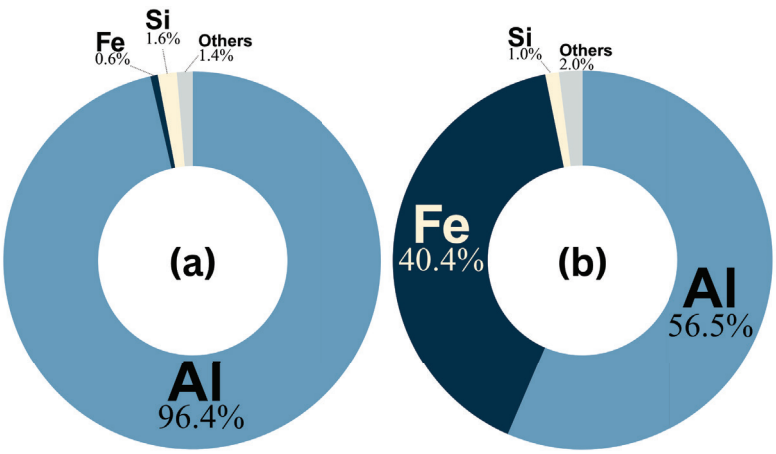

Figure 1 *Elemental composition of (a) scrap Al and (b) synthesized Al–Fe bimetal.*

Solution pH also increased concurrently from 2.12 to a maximum of 5.7 at the maximum conditions (Figure 2), indicating that the removal process consumed acidity and promoted hydroxide generation (Lien *et al.* 2019; Teng *et al.* 2023). The Al–Fe bimetal thus captures dissolved metals while partially self-neutralizing the treated solution. From a mine-water perspective, this is an important result because it suggests that the Al–Fe bimetal offers a dual function of metal capture and partial acid neutralization in a single step, reducing the downstream burden of pH correction.

Mechanistic Investigation of Cu and Zn Removal

Copper and zinc removal are governed by surface electrochemical processes activated under acidic AMD conditions. At pH ≈ 2.1, high proton activity dissolves pre-existing oxide/oxyhydroxide layers, exposing reactive Al and Fe sites. As illustrated in Figure 3, two parallel pathways then operate: (1) galvanic reduction, where Al acts as the sacrificial anode and supplies electrons to Fe-rich cathodic regions that reduce dissolved metal ions, and (2) direct reduction at exposed Al and Fe surfaces.

XPS of the reacted bimetal showed no distinct Cu 2p or Zn 2p signals initially, while Al 2p and Fe 2p regions became dominated by Al(III) and Fe(II/III) oxide/oxyhydroxide species with zero-valent Al and Fe no longer evident. As XPS probes only the top few nanometers, this corrosion-product overlayer – consistent with the observed pH rise – likely masks earlier-formed metallic deposits, especially given that Cu removal was complete well before the reaction ended. To resolve the captured metal speciation, a more concentrated Cu–Zn–Fe model solution was examined by XPS (Figure 4).

The Cu 2p spectra confirm Cu capture predominantly via electrochemical reduction, with Cu(0) on the reacted surface and Cu(I) (Cu2O) suggesting a sequential Cu2+ → Cu+ → Cu0 route; the Cu(II) signal (CuO) is attributable to subsequent oxidation of deposited Cu during the prolonged reactive period rather than to capture itself. Zn showed a different speciation: Zn(0) confirms reductive deposition, but the simultaneous Zn(II) signals (likely ZnO and Zn(OH)2), together with Al/Fe oxide–oxyhydroxide enrichment in the Al 2p and Fe 2p spectra, indicate a mixed mechanism of reduction plus secondary co-precipitation with Al–Fe corrosion products — a well-documented Zn-removal pathway in wastewater systems. Overall, Cu capture is dominated by electrochemical reduction, whereas Zn proceeds through combined reduction and surface-mediated retention, consistent with the faster, more favorable Cu removal (Wang *et al.* 2014; Passos *et al.* 2021).

Preliminary investigation of bimetal reusability and implications for downstream recovery

A preliminary reusability test applied a single batch of Al–Fe bimetals to five successive sets of fresh synthetic AMD (20 g/L, 120 min per cycle). Cu removal remained consistently high across all five runs, whereas Zn removal began to decline after the third cycle. This divergence is likely driven by progressive surface passivation: with each cycle, deposited metallic Cu and accumulating Al/Fe corrosion products build up on the

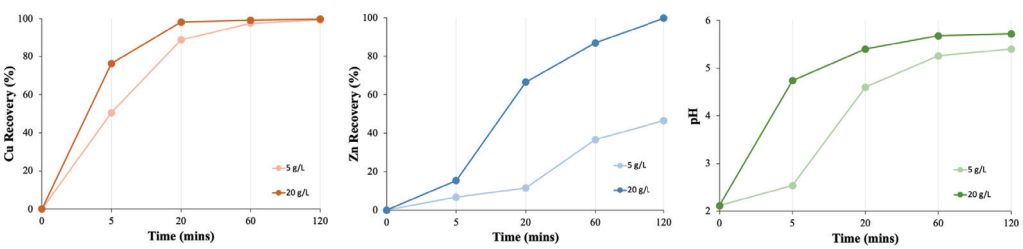

Figure 2 *Removal of Cu and Zn, and pH changes in varying bimetal dosages and contact time.*

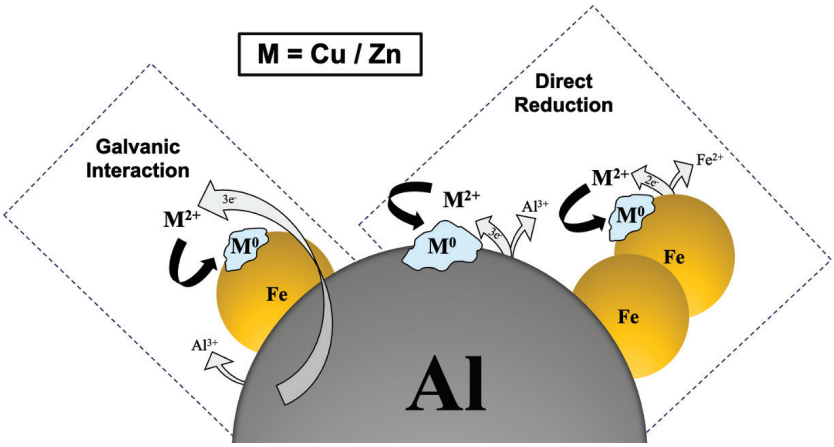

Figure 3 Schematic illustration of the surface electrochemical processes in the Al–Fe bimetal.

bimetal and gradually mask the reactive Al^0 and Fe^0 sites that drive galvanic activity. Cu can still be reduced because residual Fe at the surface remains sufficiently reducing toward Cu^{2+} even as the galvanic system weakens. For Zn, however, removal depends on the combined action of galvanic reduction and co-precipitation with freshly formed Al/Fe oxyhydroxides – both of which are diminished once the surface is passivated – explaining why Zn is the first to drop off with repeated use.

The kinetics and speciation observed for Cu and Zn point to several possibilities for post-recovery valorization that future work can pursue using this study as groundwork. One possibility lies in the kinetic window between the two metals: Cu reached complete removal within 20 min while Zn still required 120 min at the same dosage, suggesting that contact time could be used as a selectivity lever – a short-contact stage to preferentially load Cu, followed by a longer-contact stage on a separate batch to target Zn. Another possibility is to design downstream processing around the differing surface speciation of the loaded metals – Cu captured largely as Cu(0) on a discrete metallic layer, and Zn distributed between Zn(0) and Zn(II) phases co-precipitated with Al/Fe oxyhydroxides – with leaching and recovery schemes tailored to each form. These directions can be pursued in parallel, alongside regeneration strategies that restore reactive sites and testing on

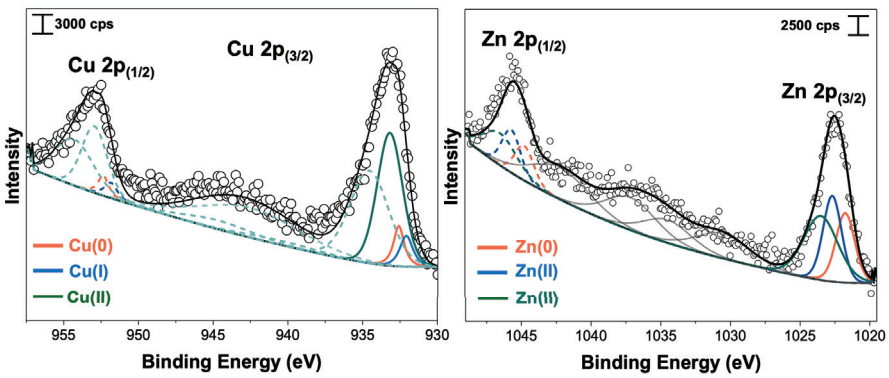

Figure 4 XPS narrow-scan spectra of the loaded Al–Fe bimetal after reaction with model solutions, acquired at Cu 2p and Zn 2p regions.

real AMD matrices with techno-economic evaluation to assess practical deployment.

Conclusions

The broader significance of this work lies in its dual-waste reuse concept. By simultaneously repurposing scrap aluminum filings and applying them to acid mine drainage for metal capture, this work demonstrates a concrete pathway toward circular mine water management. Unlike conventional AMD treatment approaches that generate mixed sludge of limited commercial value, the Al–Fe bimetal captures Cu and Zn onto a concentrated solid substrate amenable to downstream recovery while partially self-neutralizing the treated solution, reducing the downstream burden of pH correction. These characteristics make the approach particularly attractive for application in active or legacy mining sites in developing regions where access to high-purity reagents and complex infrastructure is limited. Taken together, these findings establish scrap-derived Al–Fe bimetals as a promising AMD treatment platform with downstream recovery potential. Future work should focus on isolating the captured metals as separable, usable products, alongside testing on real AMD matrices, extended reusability assessment, and techno-economic evaluation for practical deployment.

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