

# Passive treatment experiments including slag reactor and As adsorption reactor for mine drainages in Peru

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# Abstract

Drainages from two mines in the Ancash region of Peru were enriched with Al, As, Fe, and Mn, and Zn. Both pilot-scale and laboratory-scale slag reactors were employed to remove Mn and Zn. The column system effectively reduced Mn and Zn concentrations to <0.1 mg/L for both mines, with a residence time of 14.4 hrs in the slag reactor. Additionally, As was removed to <0.09 mg/L, likely due to coprecipitation and adsorption by Fe, even in the absence of a dedicated As adsorption reactor. These results suggest efficacy of the complex passive treatment system to treat Al, As, Fe, Mn, and Zn as well as possible utilization of coprecipitation-adsorption by Fe to reduce As and Zn concentrations in passive treatment system. The adsorption efficiency can be further enhanced by design improvement in the future.

Keywords: Slag reactor, arsenic adsorption, manganese treatment, Peru, mine drainage

# Introduction

Peru is the second largest producer of Cu and Zn in the world. Its porphyry copper ores and hydrothermal multimetal ores are rich in various metals, which can lead to water contamination by Al, As, Cd, Fe, Mn, and Zn. To address this, eco-friendly, low-carbon, and cost-efficient passive treatment technologies are crucial for metalliferous mines.

# Methods

Among several candidate mines, two metalliferous mine drainages of El Triunfo 1 (ET) and Santa Teresita (ST) in the Ancash region, Peru, were selected. The ET adit drainage exhibited high concentrations of Al (13.5 mg/L), As (1.69 mg/L), Cd (0.084 mg/L), Fe (31.3 mg/L), Mn (7.73 mg/L), and Zn (21.0 mg/L). Meanwhile, the ST adit drainage had high concentrations of Al (15.1 mg/L), Cu (0.49 mg/L), Fe (11.4 mg/L), Mn (43.1 mg/L), and Zn (6.79 mg/L). Both pilotscale and laboratory-scale slag reactors were employed to remove Mn and Zn, following the treatment of Al and Fe by SAPS and oxidation pond system, for both mines.

Columns to treat ET drainage consisted of SAPS, VFR (Vertical Flow Reactor), and slag reactor, while the columns for ST drainage consisted of SAPS and slag reactor. Diameter and height of each column was 50 mm and 300 mm, respectively, and the flow direction was downward. SAPS column had a upper organic matter layer of 45 mm and a lower limestone layer of 150 mm. Volume of water in the limestone pore space was 147 mL. VFR column had a limestone layer of 45 mm and a open water layer of 175 mm. Total volume of water in the open water and limestone pore was 417 mL. Slag reactor column had a layer of steel slag mixed with limestone of 150 mm. The volumetric mixing ratio between the steel slag and limestone was 4:6. Porosity and pore volume of the mixed substrate were 36% and 141 mL, respectively. The outflow tube of each column was hung to the column at

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a specific level to maintain the water level in the column. ET and ST drainages flowed into each column set using a peristaltic pump.

Additionally, As adsorption reactor was applied for ET drainage. The drainage was pretreated using limestone and steel slag to decrease Al, Fe, Mn, and Zn concentrations. The adsorbent used was CMDS-bead, which was a bead-shape adsorbent made from Fe-rich sludge from a coal mine drainage treatment facility in South Korea. Upward flow was applied with empty bed contact time (EBCT) of 20 min.

Pilot-scale treatment facilities for both mines consisted of SAPS 1 - Settling pond/ VFR 1 – SAPS 2 – Settling pond/VFR 2 – Slag reactor – Aerobic wetland – As adsorption reactor. Two consecutive series of SAPS and settling pond/VFR were applied due to the excessive acidity at both mines. Settling ponds were designed to be able to be converted to VFR. After accumulation of Fe-rich sludge, the flow will be changed from horizontal to vertical direction to induce enhanced adsorption of As by the Fe sludge layer. Aerobic wetland was installed to decrease pH again after the slag reactor.

The inflow and outflow samples for the column sets and each pilot-scale treatment unit were collected and actual flow rates were measured using a bucket-and-stopwatch method. Electrical conductivity (EC), temperature, pH, and dissolved oxygen (DO) concentrations were analyzed using Hach HQ2200 multimeters immediately after sampling. Alkalinity was determined using Hach AL-DT digital titrator. Collected samples were filtered using 0.45 µm syringe filter papers and samples for cation analysis were acidified to pH < 2 using concentrated nitric acid. Cations were analyzed using a inductively coupled plasma optical emission spectroscopy (ICP-OES) at the Certimin, Lima, Peru. Anions were analyzed using a ion chromatography (IC) at the Certimin, Lima, Peru. Relative standard deviations (RSD) were less than 5% for ICP-OES and IC analyses.

# **Results and discussion**

# Column experiments

The column system could decrease Mn and Zn concentrations to <0.1 mg/L for both

mines, with a residence time in the slag reactor of 14.4 hrs. Effluent standard in Peru for Zn concentration is 1.5 mg/L, and stream water quality standard in Peru for Mn concentration is 0.2 mg/L. The effluents met those standards with a much higher efficacy. Mn and Zn may have been precipitated as hydroxides and carbonates in the slag reactor which may have increased pH sufficiently. The pH values of final outflow samples were 7.7–8.8, which was decreased again by dissolution of atmospheric CO<sub>2</sub> after the slag reactor.

Concentrations of Al, Cd, Cu, and Fe decreased to <0.8, <0.001, <0.01, and <0.2 mg/L, respectively. These values were far less than the effluent standard concentrations in Peru for Cd, Cu, and Fe, which are 0.05, 0.5, and 2 mg/L. Moreover, As was removed to <0.09 mg/L, which was less than the effluent standard of 0.1 mg/L in Peru. This was likely due to coprecipitation and adsorption by Fe, even without an As adsorption reactor.

Additionally, in the adsorption column experiment for As removal, the reactor successfully decreased As concentrations from 1.69 mg/L to <0.008 mg/L.

# *Pilot-scale experiments*

At ET mine, treatment efficiencies were assessed after five months of the pilot-scale system installation. At the SAPS 1, pH increased from 4.70 to 6.37, to decrease Al concentration from 7.93 to 0.07 mg/L. Zn concentration also decreased from 19.00 to 1.32 mg/L. As the pH was not high enough to precipitate Zn hydroxides, precipitation of Zn carbonates and sulfides and/or adsorption onto Fe (oxy)hydroxides and coprecipitation with Fe which decreased from 92.6 mg/L to 41.8 mg/L may have decreased Zn concentrations. At Settling pond 1, Fe was efficiently oxidized to be 0.12 mg/L. During this process, As concentration decreased from 2.04 mg/L to 0.35 mg/L by adsorption and/or coprecipitation by Fe. At the slag reactor, Mn concentration decreased from 4.3 to 2.5 mg/L at pH of 8.54. As the DO concentration and Eh of slag reactor inflow were only 2.25 mg/L and -5 mV, the reducing condition may have inhibited the oxidative treatment of Mn. Organic matter



still flowed out from the organic matter layer of SAPS 2 to make reducing conditions in following treatment units.

# Conclusion

Given the broad spectrum of contaminants addressed in these mine drainages, the passive treatment technology demonstrated here can potentially be expanded to treat diverse mine drainages contaminated with Al, As, Cd, Cu, Fe, Mn, and Zn. The results in this study suggest efficacy of the combined passive treatment system as well as the possible utilization of coprecipitation-adsorption by iron to reduce As and Zn concentrations in passive treatment system. The As adsorption efficiency by Fe in mine drainages can be further enhanced by design improvement in the future.

#### Acknowledgements

This work was supported by the Korea International Cooperation Agency (KOICA) through a project (Improving Peru's Mine Closure and Mining Environmental Liabilities Remediation Procedure in Support of SDG Achievement). The authors gratefully acknowledge the contributions of the people at Ministry of Energy and Mines, Peru, for conducting experiments.