

A continuous pilot-scale system using coal-mine drainage sludge to treat acid mine drainage contaminated with high concentrations of Pb, Zn, and other heavy metals

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Introduction

Acid mine drainage (AMD), a highly acidic aqueous solution, is formed through the chemical reaction of surface and shallow subsurface water with rocks containing sulfur-bearing minerals to give sulfuric acid. Heavy metals can then be leached from rocks through contact with the acid. When AMD mixes with groundwater, surface water, and soils, it may have harmful effects on humans, animals, and plants. Specifically, in Pb–Zn mines, Zn(II) is released at high concentrations in AMD compared to other toxic heavy metals such as Fe(II), Fe(III), Al(III), Cu(II), Cd(II), and Pb(II). The oxidation of pyrite (FeS_2) and sphalerite (ZnS) in tailings of abandoned mines can occur spontaneously and may be catalyzed by iron oxidizing bacteria and Fe(III), resulting in the production of high acidity and Zn(II). Since high concentrations of Zn(II) are also observed in industrial wastewater discharged by metal processing, battery manufacturing, etc. [1], Zn(II) concentrations in surface, ground, and potable water are strictly regulated worldwide [2].

By comparison to AMD released from metallic mines, the AMD that occurs at both operating and abandoned coal mines is generally

characterized by a low pH and often by high concentrations of dissolved metals such as Fe, Al, and Mn but low concentrations of heavy metals such as Zn(II), Cu(II), Cd(II), and Pb(II) [3]. However, the flowrate of AMD in coal mines is higher compared to that in metallic mines [4]. Typical processes for treating AMD from coal mines rely on the removal of dissolved metals via oxidation, precipitation, and separation. One of the most significant problems in the treatment of coal mine drainage is the large volumes of sludge. Moreover, the ultimate disposal of AMD sludge is difficult because of the low economic value of the waste sludge, substantial difficulties in dewatering, and the high cost of offsite haulage [5–7].

As an alternative option, the sludge volume could be reduced by electrolysis followed by aeration, which has been developed and adopted for treating AMD onsite in South Korea. Simply put, the electrolysis process treats AMD by reducing hydrogen at the cathode and oxidizing ferrous to ferric ions at the anode. This technology is applicable when the stoichiometric concentrations of hydrogen and ferrous ions are almost the same [8]. Since the oxidation of ferrous ions in AMD occurs without the addition of a neutralizing agent, the electrolysis process reduces the volume of sludge and operating costs [9]. The sludge is characterized mainly by amorphous micron- and submicron-sized iron oxide/hydroxide particles containing sulfate, and generally has a high surface area as well as numerous functional groups for removing dissolved trace metals through adsorption and co-precipitation [10–13]. To date, however, very little work has been reported on the removal mechanism of heavy metals.

Previously, the authors have aimed to elucidate the main mechanism of Zn(II) removal by CMDS produced from a full-scale electrolysis treatment plant by conducting a series of batch tests, such as isotherm, kinetic, and edge (pH effect) tests. In addition,

spectroscopic analyses such as zeta potential, XRD, FT-IR, and SEM were conducted [9]. The results of the XRD analysis showed CMDS to have a heterogeneous composition with the main components being calcite (30%, w/w) and sulfate complexed iron (oxy)hydroxide (70%, w/w). The batch tests showed that the negatively charged groups coupled to the sulfate ions, FeOH-SO_4^{2-} , had an electrostatic attraction to Zn(II) . However, the results of the FT-IR analysis showed that Zn(II) might be significantly precipitated as carbonate compounds, even though the Zn(II) removal by complexation with goethite could not be confirmed. Precipitation as carbonates may have occurred due to the solubility product (K_{SP} , $10^{-3.01}$) of ZnSO_4 being much higher than that of ZnCO_3 (K_{SP} , $10^{-10.8}$) or $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ (K_{SP} , $10^{-14.85}$) [14, 15].

In this study, a treatment system consisting of a continuously stirred tank reactor, settling tank and sand filter was constructed and operated to determine the treatment efficiency for an acidic metallic mine drainage. For the tests, actual AMD from a Pb-Zn mine was applied to find the effect of the operating parameters, such as CMDS injection concentration and retention time. The ultimate objective is to optimize the main parameters needed for designing a full-scale treatment plant.

Material and methods

2.1. Analyses of CMDS

CMDS was prepared by drying sludge taken from a full-scale treatment facility, in which an electrolysis process had been adapted to treat acidic drainage coming from a coal-mine adit in South Korea. The CMDS was dried at 25°C in open air for 5 days. The specific surface area of the CMDS was analyzed with a surface analyzer (ASAP 2010, Micromeritics Inc.). After shaking the CMDS in deionized water at a ratio of 1–5, the sludge pH was measured

with a pH meter (Thermo Orion model 420A+). The concentrations of heavy metals in all samples were measured using an inductively coupled plasma atomic emission spectrometer (ICP-AES, 5300DV, PerkinElmer).

2.2. System set-up and operation

Actual AMD was sampled onsite from the effluent of settling tanks for treating acidic drainage from a Pb–Zn mine in South Korea. Table 1 shows the chemical properties of the drainage used in this study. The wastewater was acidic (pH 2.65) and had a high acidity (288 mg L⁻¹). The concentrations of the cationic metal species Cu(II), Pb(II), Zn(II), and Fe(III) were 25.5, 0.091, 44, and 98 mg L⁻¹, respectively, while that of the sulfate ions was 2550 mg L⁻¹. After Fe(III), Zn(II) had the highest loading (44 times the regulatory limit) among the heavy metal species. Fig. 1 and Table 2 show a schematic and the properties of the treatment system, consisting of a stirring tank reactor [volume 2 L, diameter (D) 120 mm× height (H)177 mm], a settling tank (volume 3.3 L, D 120 mm×H 292 mm) and a sand filter (volume 2.7 L, D 50 mm×H 1400 mm). In the sand filter, the grain size of the sand was in the range 0.25–0.5 mm. In the first test, the following operating conditions were setup for the pilot system: the influent flow of AMD was 8 L day⁻¹, and 560 g CMDS (dry wt. basis) was introduced into the stirring tank reactor (2 L, concentration 280 g L⁻¹). The retention times for the stirring tank reactor, settling tank, and sand filter were 0.25, 0.41, and 0.34 days, respectively. In this test, influent and effluent samplings in the settling tank and sand filter were conducted for 70 days. The flowrate of sludge return was set to be the same as that of the main system, in order to sustain a constant concentration of sludge in the stirring tank reactor. In the second tests, authors tried to find the optimum operational conditions for the continuous treatment system by testing different amounts (80–560 g L⁻¹ at stirring tank

reactor) of CMDS and altering the flowrate (6–30 L day⁻¹).

2.3. Kinetics and treatment efficiency

Since the removal mechanisms of Zn(II) involve mainly the stirring tank reactor and the settling tank, in which most of the CMDS is retained, the value of the total rate constant (K_{total}) was obtained for the combined system of the stirring tank reactor and settling tank. The K_{total} value was also calculated using the equation below. If all parameters are assumed to be constant, except for the metal concentrations, this system follows a pseudo-first order reaction [16],

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where $V_{reactor}$, Q_{total} , $C_{influent}$, and $C_{effluent}$ are the reactor volume, flowrate, and metal concentration of influent, and metal concentration of effluent, respectively.

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<http://www.ncbi.nlm.nih.gov/pubmed/22421342>

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