

# Potential application of sludge produced from coal mine drainage treatment for removing Zn(II) in an aqueous phase

Mingcan Cui · Min Jang · Sang-Hyun Cho · Jeehyeong Khim

## Introduction

Acid mine drainage (AMD) could not only pollute natural environments such as surrounding soils, and surface- and groundwater, but it could also have sequential toxic effects on crops and humans through contamination (Jung [1994](#)). The most environmentally effective techniques available for mitigating AMD are neutralization and biological processes (Watten et al. [2005](#)). In order to select an appropriate technology for AMD, several parameters such as the chemical characteristics of the AMD, the quantity of water needed for the treatment, local climate, topographic characteristics of the on-site location and the expected life of the treatment plant should also be considered. The chemicals usually used for neutralizing AMD include limestone, hydrated lime, soda ash, caustic soda, ammonia, calcium peroxide, kiln dust and fly ash (Watten et al. [2005](#); Sibrell et al. [2003](#)). Although AMD itself could be treated by a neutralizing chemical, the chemical process usually results in the production of voluminous sludge; disposal of this sludge could create further environmental problems and additional costs. Particularly, the treatment of coal mine drainage results in a high volume of sludge because the drainage volume of coal mine is higher than that of metallic mines. In addition to the high volume of sludge, the high cost of conventional cleanup technologies for the sludge has produced economic pressure and has caused engineers to search for creative, cost-effective and environmentally sound

ways to treat sludge (Bulusu et al. 2007). Compared to conventional treatment, electrolysis is a more effective method that reduces the acidity of mine drainage without using a neutralizer such as lime or limestone (Chartrand and Bunce 2003). Accordingly, as an advantage, the electrolysis process could produce a lower volume of sludge because a neutralizer is not added. Electrolysis functions with two cells (anode and cathode), in which the hydrogen ion ( $H^+$ ) is reduced to  $H_2$  in the cathode while  $Fe(II)$  is oxidized to  $Fe(III)$  in the anode. Electrolysis is known to be practical when the stoichiometric concentrations of  $H^+$  and  $Fe(II)$  in mine drainage are nearly equivalent. In this study, the sludge produced by the electrolysis for treating coal mine drainage was designated as coal mine drainage sludge (CMDS). As an alternative of sludge treatment, the reuse of CMDS as a material in the water treatment process could be a valuable option. The following generalized mechanisms of sludge production are helpful to understand the possibility of sludge reuse as a material. Ordinarily, AMD usually contains high concentrations of sulfate and  $Fe(II)$ . The CMDS that results from the treatment of coal mine drainage consists mainly of iron (oxy) hydroxide such as jarosite  $[KFe_3(OH)_6(SO_4)_2]$ , schwertmannite  $[Fe_8O_8(OH)_6SO_4]$ , goethite ( $\alpha$ - $FeOOH$ ), ferrihydrite ( $Fe_2O_3 \cdot 1.8H_2O$ ) or magnetite ( $Fe_2O_3$ ), while containing low levels of other heavy metals (Marcello et al. 2008). As the main parameter, the pH and sulfate concentration are important to determine the identification of Fe precipitates for not only the naturally occurring sludge, but also for the sludge produced from a treatment facility. Jarosite can be formed with pH 3 and high concentrations of sulfate, while ferrihydrite and goethite can be made at a neutral pH. Schwertmannite could be precipitated at pH 3 \* 4 (Jonsson et al. 2005). The structures of jarosite and schwertmannite are known to be unstable but could be transformed to more stable forms of

iron precipitates such as goethite or magnetite (Jonsson et al. 2005). Accordingly, due to amorphous iron compounds, the sludge could have amphoteric characteristics of surface functional groups that can remove heavy metals (e.g. Cd, Cu, Pb, Zn) and anionic metalloids (e.g. As and Se) in an aqueous phase. However, more extensive characterization is needed to study the stability and removal mechanism for heavy metals.

In particular, the removal of heavy metals into iron compounds is thermodynamically favorable for iron compounds among other materials. For example, the adsorption of cationic heavy metal species on the hydroxyl group of goethite ( $\alpha$ -FeOOH) has been found as an endothermic reaction. Thus, the adsorption capacities and equilibrium constants increase as the temperature increases (Angove et al. 1999; Harter 1992; Darren et al. 1993; Rodda et al. 1993, 1996a, b; Trivedi and Axe 2000). The removal of heavy metals by goethite has also been studied at various pH levels (Nita et al. 2007).

In this study, the objective is to study the possibility of sludge produced from a full-scale electrolysis process for treating coal mine drainage as a material in the field of environmental application. This is achieved through not only investigating physico-chemical properties, but also by analyzing the results of sorption isotherms and sorption kinetics, which were also compared with other referenced values of conventional media.

## Materials and methods

### Materials

In this study, CMDS was simply prepared by drying the sludge taken from an electrolysis treatment facility at 25 °C. The facility has been operating to treat acidic mine drainage flowing from a mine edit of coal mine in Kangwon, South Korea.

### Batch sorption experiments

The sorption isotherms and sorption kinetics were conducted using the suspension of CMDS in either synthetic water contaminated with Zn(II) (40 mg L<sup>-1</sup>) or mine drainage [main contaminants: Zn(II) (40 mg L<sup>-1</sup>) and Cu(II) (25 mg L<sup>-1</sup>)](see Table 1) sampled from an abandoned gold mine. The obtained data of sorption isotherms and sorption kinetics were fit using the Langmuir sorption isotherm and the pseudo-second order kinetic model, respectively. The equation of the Langmuir sorption isotherm and pseudo-second order kinetic model was as follows:

*Please refer to the full text*

where  $q_e$  is the amount of solute adsorbed per unit weight of adsorbent (mg g<sup>-1</sup>),  $C_e$  is the equilibrium concentration of solute in the bulk solution (mg L<sup>-1</sup>),  $q_{max}$  is the maximum adsorption capacity (mg g<sup>-1</sup>),  $b$  is the Langmuir constant related to the energy of adsorption,  $k_2$  is the pseudo-second order kinetic constant,  $t$  is the time (min),  $q_t$  is the adsorbed quantity of metal ions per gram of media at any time (mg g<sup>-1</sup>).

### Mineralogical analysis

The particle size analysis for the sample taken from the suspension of CMDS was conducted using a particle size analyzer (LMS-300, SeishinEnterpriseCo. Ltd., Tokyo, Japan) to find out whether CMDS has a seasonal variation in particle size. The elemental composition of the CMDS taken at different seasons was also determined with an X-ray fluorescence (XRF) spectrometer (XRF-1700, Shimadzu, Japan). The XRD analyses were conducted for the selected freeze-dried powdered samples of CMDS by use of a PANalytical X'Pert Pro diffract meter (fitted with an X'Celerator) with a Cu Ka radiation source at a scan speed of 2.5\_ min<sup>-1</sup>. The

phase identification of CMDS was also carried out by means of the X'Pert accompanying software program High Score Plus and the reference intensity ratio method (RIR method) ICDD PDF-4<sup>?</sup> database (USA, 1999). Through looking at the binding energy of specific peaks, the mineral phases in the CMDS were also determined by XPS (Physical electronics PHI 5800 ESCA System), which has a monochromatic Al Ka (1486.6 eV) and anode (250W, 10kV, 27mA) X-ray source. The specific surface area of CMDS was analyzed by the Brunauer-Emmett-Teller (BET, ASAP 2010, micromeritics Inc., USA) adsorption method, which uses nitrogen gas (Quanta chrome Instruments, Sutosorb-1-C Chemisorptions-Physisorption Analyzer). The pH of CMDS was measured by the EPA method 9045c after preparing a suspension (L/S = 1:1) with distilled (DI) water. The pH of suspension was measured with a pH meter (Thermo Orion model 420A<sup>?</sup>). Heavy metals in solution were analyzed by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, 5300DV, Perkin Elmer, CETA, USA). The pH<sub>IEP</sub> of CMDS was found using a ZetaMeter (ZetaMeter Inc., Model 3.0<sup>?</sup>, USA), and the toxicity characteristic leaching procedure (TCLP) for CMDS was conducted by EPA method 1311, respectively. Specifically, the purpose of TCLP was to find out the stability of CMDS through analyzing the extracted toxic elements such as Pb, Cu, As, Hg, Zn, and Ni. Further mineralogical analyses were performed on gold-coated samples by a SEM(JSM5800LV, JEOL, Japan) associated with an energy dispersive X-ray system (EDS, Link AN 10/55S). The FT-IR absorption spectra of the samples in the 400 \* 4,000 cm<sup>-1</sup> spectral range were obtained with a FT-IR spectrometer (FT-IR 6200, JASCO, USA). The IR absorption measurements were done using the KBr pellet technique. In order to obtain good quality spectra, the samples were crushed in an agate mortar and micro-size particles were

obtained for FT-IR analysis.

Full text is available at :

<http://www.ncbi.nlm.nih.gov/pubmed/21063752>

<http://link.springer.com/article/10.1007/s10653-010-9348-0>