Comparison of As, Ni, Zn, Cd, and Pb removal using treatment agents at mine area

Jaeyoung Choi[a] *, Hyun-sik Yun[a]

[a]Korea Institute of Science and Technology (KIST)-Green City Technology Division, Seoul, South Korea

Summary

This study investigates As, Ni, Zn, Cd, and Pb removal onto Fe oxide minerals, limestone, black shale, and dolomite from mine wastewater. Natural materials or waste products with a high capacity for heavy metals can be obtained and employed of with little cost. For investigating the neutralization capacity, the change in pH, Eh, and EC as a function of time was quantified. Of the treatment agents, concrete showed that the high neutralization efficiency for abandoned mine drainage (AMD) and maintained the pH value above 11. The adsorption of heavy metals by the samples was influenced by compositions of treatment agents. The experimental results of desorption revealed that when the adsorption or precipitation occurs, there was no significant releasing from all treatment agents. In this study, the results suggest that concrete can be used successfully in the treatment of mixed metal-contaminated wastes at mine area.

Introduction

Heavy metals pollution has become one of the most serious environmental problems [1]. With the rapid development of various industries, wastes containing metals are directly or indirectly discharged into the environment increasingly. After releasing from industrial wastes area, metals possibly be transported by groundwater and surface water away from the source.

For the last scores of years, several remediation technologies have been developed for removing heavy metal from subsurface environment such as precipitation, adsorption and complexation of metal, electrochemical remediation, oxidation and hydrolysis, neutralization, ion exchange and solvent extraction, bioaccumulation, reverse osmosis [2-4].

Among these methods, adsorption and ion exchange using natural, synthetic and modified inorganic and organic solids have been explored. In this group, natural minerals act as potential adsorption agents for heavy metals due to their low cost, high abundance, easy manipulation, and harmlessness to the environment. For such purpose a diversity of processes such as chemical precipitation, adsorption on selected materials and precipitation can be applied. Alternatively, any other conventional solid has been proposed as source for metallic cations removal from wastewater.

In this study, the sorption relationship between wastewater containing heavy metals and natural and synthetic materials based on same solution composition and aging conditions was investigated. The choice to investigate As, Cd, Ni, Pb, and Zn is based on the reasoning that these metals are some of the

most commonly occurring base metals in wastewaters including mine discharge. The results of this study will provide valuable data to assist in the selection of remediation conditions by offering a guide to metal removal in a variety of common minerals and synthetic materials.

Theory and/or Method

2.1. Preparation of treatment agents

Six treatment agents, white limestone (WLS), dolomite (DM), goethite (GT), hematite (HT), black shale (BS), and Jumunjin sand (JS), were selected based on their low cost, high abundance, easy manipulation, and harmless to the environment.

2.2. Column Experiments

Miscible displacement (flow) experiments were conducted at room temperature (295.5 ± 0.5 K) and constant ionic strength (0.01 M). Treatment agents filings were then uniformly mixed with Jumunjin sand (79.55 % SiO_2; surface area, 0.05 m^2/g; 0.5-0.7 mm in diameter) and packed into polyvinylchloride (PVC) columns (30 cm long, 10 cm in diameter). Each sand-adsorbent mixture was first homogenized and then dry packed under the same pressure for each sample and 0.5 m filters were placed at both ends of the column to prevent any carry over of particles. The ratio of each treatment agents filings to Jumunjin sand illustrated on Table 2. To study heavy metal uptake at different treatment agents, 10 mg/L each of As, Cd, Pb, Zn, and Ni in multi-element solution (i.e., total metal concentration 50 mg/L) was passed through each column for 90 days. The columns were slowly flushed from the bottom and mixed heavy metal solution was introduced to each columns at a specific discharge of 4.3 ml/h. Effluent samples were collected with small vial once a day for 10 min at same time for measuring pH, redox potential (Eh), electric conductivity (EC), and metal concentrations. All water samples were quantified by Inductively Coupled Plasma Emission Spectroscopy (Varian Co., ICP-OES 730).

2.3. Desorption Experiment

Following the adsorption experiment, subsequently, metal desorption was quantified with followed by rinsing ultra pure water for 30 days with flow rate of 4.5ml/h. As same as column experiments, effluent samples were collected once a day and measured for collecting data which was conducted in a similar fashion on the same column.

2.4. Chemical speciation of heavy metals

MINEQL+ [5] was used to quantify aqueous speciation of metals as a function of pH. The chemical speciation of the metals was modeled because the hydrolysis behavior of metal ions could affect adsorption process (Fig. 1). The dynamic equilibrium between heavy metals in solution and that adsorbed on the solid phase of the adsorbents depends on many factors including pH and ionic strength, aqueous-phase speciation of metals, the chemical nature and surface area of mineral and organic sorbents, and the presence of competing ions [6].

Examples

The amounts of residual contaminants were investigated by reporting each metals concentration before, during and after treatment with the dosing agent (Fig. 2). The heavy metal removal from aqueous solutions is quite a complicated process, consisting of ion exchange and adsorption and is likely to be

accompanied by precipitation of metal hydroxide complexes on active sites of the particle surface. The actual composition of metal species in solution is highly dependable on the pH of the water and more soluble metal ions are found at the very low pH values typical for acid water.

In the case of As, only GT produced a steep decrease during the first 40 day, followed by a slight progressive increase for the rest of the time intervals, although no complete removal of As was reached (Fig. 3). DM, HT, JS, and WLS produced a very steep increase within the first 24 h, followed by an inconsistent trends characterized by concentration fluctuations and a reversible behavior. Otherwise, BS was used, lower residual concentrations of As were obtained (< 0.8 C/C_0 ratio) than that shown by DM, HT, JS, and WLS, although with an inconsistent behavior of its trends between 38 and 42 day (Fig. 3). In the case of Cd, GT produced a steep decrease during the first 24 h, after which plateau values were reached with very low residual concentrations of the rest of the time intervals, with an almost complete removal. BS and JS show a lower efficiency than that shown by DM, HT, and WLS, although a sudden increase occurred after 40 days and with an inconsistent behavior and significant fluctuations for the rest time intervals.

Conclusions

As a result, for each of the 6 agents, only GT reached sufficiently low values of Eh, alkaline pH value, low heavy metal concentrations after treatment. However, adsorption ability of agents for heavy metals is very different due to the dissimilar element character. In addition, the order of adsorption ability of heavy metals onto the various components is inconsistent, which might indicate that different sorption mechanisms occurred simultaneously rather than only one sorption mechanism works in the sorption process of heavy metals onto components. In this study the effect that various particle sizes of the treated agents have on the neutralization rate is not investigated. In general, an increased surface area resulted in an increased neutralization rate, as can be expected. To verify these conclusions further studies are needed, which are based on comparisons with different flow rate, redox chemistry with coexisted ions, and which are competed with other inorganic cations and anions, and organic materials coexisting in contaminated subsurface environment.

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