Stabilization of available arsenic in highly contaminated mine tailings using iron

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1. Introduction

Arsenic is commonly found in sulfur minerals along with precious metals. Arsenic species released from sulfur-containing minerals during weathering processes undergo oxidation-reduction, precipitation-dissolution, adsorption-desorption, and organic and biochemical methylation reactions, all of which control the behavior of arsenic in the environment (1). The objective of this study is to evaluate the stabilization of available As in contaminated mine tailings using the addition of iron compounds. Inorganic solidification/stabilization processes have been studied to reduce solubility of As in solid waste, using inorganic binders such as cement, lime, and pozzolanic materials (e.g. 2). Recent investigations of As sorption on amorphous and crystalline iron hydroxides illustrate the potential for As attenuation via interaction with these mineral surfaces (e. g. 3). The sequential extraction of contaminated soils by Dudas (4) also showed that arsenic was primarily associated with crystalline and amorphous oxides of iron. Other studies have implicated amorphous iron and aluminum as preferential adsorbents of arsenic (5) and iron oxides in general for the sorption of arsenite (6). Iron can also form insoluble iron-arsenic compounds such as $FeAsO_4$.

2. Materials and Methods

Tailings samples were collected from two abandoned metal mines in South Korea, Myoungbong Au-Ag mine and Daduck Au-Ag-Pb-Zn mine. The pH, organic matter content, and sand, silt and clay size distributions of the tailings were determined. Total concentrations of As, Cd, Cu, Pb, and Zn were determined by aqua regia digestion and USEPA method 3050. Toxicity characteristic leaching procedure (TCLP, USEPA 1311 method), synthetic precipitation leaching procedure (SPLP, USEPA 1312 method), 1 N HCl extraction, and NaOCl extraction were conducted to estimate the quantity of available As in the tailings. A modified version of the sequential extraction analysis set by Tokunaga *et al.* (7) was employed to estimate the bonding strength and chemical speciation of As in the tailings. Extraction results were focused on the weakly bonded As fraction that is assumed to be related to available As. Thus, this analysis was also used to evaluate the efficiency of stabilization for available As after treatment experiments.

Amorphous iron precipitates were created to stabilize the available As in the tailings. 20 ml of ferrous or ferric sulfate solution at several different concentrations (20 to 100 mmol) were added to 2 g of tailings; pH was adjusted to the range of 3 to 6 by NaOH or Ca(OH)$_2$. Following this, the mixture was shaken at 30 rpm for 2 hours and centrifuged. Concentrations of As and Pb in supernatant filtered through 0.2 m pore sized membrane filter were measured. NaOCl extraction and sequential extraction were conducted on the treated tailings to examine change in As availability. To examine the fate of As onto precipitated amorphous iron, adsorption/ co-precipitation tests were performed with synthetic As and Fe solutions. In these tests, four mixtures (100 mM Fe(III) + 20 mM As, 100 mM Fe(III) + 10 mM As, 20 mM Fe(III) + 20 mM As, 20 mM Fe(III) + 10 mM As) were made by mixing of 20 ml each of Fe(III) (as Fe$_2$(SO$_4$)$_3$) and As (from As$_2$O$_3$) solutions.

3. Results and Discussion

Comparing with concentrations in typical soils (6 mg/kg As) and tolerable levels (20 mg/kg As), total As concentrations extracted by USEPA 3010 were extremely high, 6,670 mg/kg in the Myoungbong tailings and 56,600 mg/kg in the Daduck tailings. The most abundant fraction of As in the Myoungbong tailings was step 5 (easily reducible oxides) fraction, which was 3,890 mg/kg and made up approximately 60% of the total As content. The next most abundant fraction was step 4 (soil organic fraction) at 1,510 mg/kg (23% of total As). On the other hand, step 5 (26,200 mg/kg of As) and step 6 (22,700 mg/kg of As) were the predominant fractions in the Daduck tailings, followed by step 7 (crystalline minerals fraction; 7,330 mg/kg of As). These three fractions made up 92% of the total As content in the Daduck tailings. Available As, which is considered as weakly bonded and easily releasable, is defined here as resulting from the first four steps of the sequential analysis. The sum of As concentrations from the first four steps was 2,085 mg/kg in the Myoungbong tailings and 1,320 mg/kg in the Daduck tailings.

The concentrations of As extracted by SPLP (1.1 mg/kg for both) and TCLP (35 mg/kg in the Myoungbong tailings and 20 mg/kg in the Daduck tailings) were less than the sum of first two extraction steps. The 5% NaOCl extractable As (1,076 mg/kg Myoungbong tailings; 612 mg/kg Daduck tailings) was located between the sum of first three steps and four steps. The 1 N HCl extractable As concentrations (4,740 mg/kg Myoungbong; 2,890 mg/kg Daduck) were much higher than the sum of first four steps, indicating that 1 N HCl can attack strongly bonded As in the tailings. Based on these results, the 5% NaOCl extraction was selected as a simple method for assessment of efficiency of stabilization treatment.

Compared with untreated tailings (control), 5% NaOCl extractable concentrations of As in treated tailings were remarkably reduced. For example, the original 5% NaOCl extractable As concentration in the Myoungbong tailings, 1,076 mg/kg, decreased to 334 mg/kg and 105 mg/kg by 20 mM and 60 mM ferrous sulfate treatment, respectively, and to 34 mg/kg and 0.2 mg/kg by 20 mM and 60 mM ferric sulfate treatment,

respectively. From these results, it is concluded that ferric sulfate treatment is more effective than that of ferrous sulfate to stabilize the available As in the tailings. To further assess the factors affecting the stabilization effectiveness, treatment experiments were conducted with different pH, base cation, and initial Fe concentration. Steep decreasing trends of 5% NaOCl extractable As with increasing initial Fe(III) concentration were observed in both treated tailings. Consistent trends with increasing pH were not found, but most of the treated tailings had the lowest As concentration at pH 6.

Sequential extraction analysis was applied to obtain information on the binding strength of As to amorphous Fe precipitates. As-containing Fe precipitates were synthesized using solutions containing aqueous mixtures Fe(III) and As(III). In the case of Fe precipitates formed from solutions containing 20 mM As, the sum of As in the first four steps were less than 20%, and approximately 50% of the As remained after step 6. In the case of 10 mM As, the sum of As in the first four steps was less than 10%; As extracted with step 7 was as high as 60%. The resulted for the extracted Fe are very different from As. Less than 1% of the Fe was extracted by the first four steps and more than 90% was released by step 7. Based on this information, the As extracted through the first four steps seems to be related to some type of adsorption reaction. On the other hand, As extracted with step 7 (50 ~ 60% of total As), which was released only by dissolution of Fe precipitate, is apparently sequestered through the formation of an Fe-As compound or co-precipitate. These results indicate that the Fe precipitate has a high capacity for sequestering As in forms that are relatively stable. In conclusion, application of amorphous Fe precipitates to As-containing mine tailings can lead to stabilization of available As. The effectiveness of stabilization was primarily related to the amount of Fe addition and to a lesser extent, the pH. After treatment, As bonded to Fe precipitate may become more stable with the passage of time.

References

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