

Sequential Washing Techniques Using Dual Agents for Arsenic-Contaminated Soil Remediation in Abandoned iron-ore

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ABSTRACT

Mining wastes and acid mine drainages produced from abandoned metal mines have released several toxic metalloid or heavy metals to ground- and surface-water systems. Especially, arsenic can be easily spread into other regions through the transport of arsenic-contaminated soils and arsenic dissolution occurred by changes in the geochemical environment to a reductive condition. Among several remediation technologies, soil washing can not only physico-chemically extract these heavy-metals or metalloids that were adsorbed or precipitated onto soils, but also reduce the volume of contaminated soils. Soil washing can also be applied to large contaminated areas due to its rapid kinetics, operational easiness, and economical efficiency. In this study, sequential washing techniques using sodium hydroxide and/or hydrochloric acid solutions were applied in an alternative mode for remediating high level of arsenic contaminated soils (designated as DC soils) that are in the abandoned iron-ore mine area. Since arsenic-contained iron-ore fines existed in this area can create coagulation and flocculation under the suspension, flocs can be easily transported to other area, creating second arsenic-contamination sites. Thus, before spreading out to other area, a rapid and effective remediation is needed to meet the arsenic regulation (6 mg kg^{-1}) that has been designed as arsenic extraction by the KST methods [designated as arsenic extraction (KST methods)] for reuse or safe disposal of arsenic contaminated soil. Through sequential extraction procedure, arsenic (87.5%) and iron (99.7%) were mostly abundant in crystalline minerals. Thus, it can be thought that most arsenic

exists in Fe-As precipitates or coprecipitates and iron exists mostly in the crystalline forms of iron oxide such as goethite, hematite, and magnetite. Soil washing by use of single agent was not effective in the remediation of the DC soils because the arsenic extractions (KST methods) were not reduced less than 6 mg kg^{-1} at any washing operational parameters such as agent concentration, ratios between solution volume and soil mass, and sequential washing. Through x-ray diffraction analysis, dried flocs were found to be composed of three dominant phases: silicate, ferric arsenate, and two-line ferrihydrite. Through charge neutralization of negatively charged colloidal particles (e.g. silicate and dissolved organic matters), coagulation and flocculation are generally occurred by cationic hydrolysis of amorphous precipitate of metal hydroxide. Primary particles of amorphous ferrihydrite formed by Fe-O-Fe polymerization of iron oxyhydroxyl monomers and dimers can be aggregated to form large flocs. Amorphous ferrihydrite was mainly produced by the oxidation of magnetite and it has been known to have high affinities for adsorbing both arsenite and arsenate because of its high surface area and the reactivity of surface functional groups. Thus, flocs can contain not only dissolved arsenic, but also fine particles of ferric arsenate-coprecipitated silicate. The pH adjustment in the first washing step using 0.2 M hydrochloric acid was mostly important to maximize cationic hydrolysis of amorphous ferrihydrite, inducing high sorption capacity of arsenic. The exclusion step of arsenic-containing flocs is thought to lower arsenic extractions (KST methods) of washed soils. Otherwise, high concentrated arsenic-containing flocs can be re-dispersed into soil, resulting in high arsenic residuals. Several trials of three sequential washing steps using single or dual agents have been conducted to have more effective ways. Among all combinations, alternative sequential washing using 1M hydrochloric acid (second washing step) and sodium hydroxide solution (third washing step) shows reliable and lower values of arsenic extractions (KST methods). To elucidate the mechanism of arsenic removal for dual agent application, kinetic tests were conducted. From the data observation, it was found that dissolved arsenic was easily readsorbed into residual soils. This result might be caused by dominant species of crystalline iron oxides that have been characterized through sequential extraction procedure. At low pH condition, the presence of positively-charged crystalline iron oxide such as goethite can easily readsorb soluble arsenic. Arsenic extractions (KST methods) of soils washed at third washing step (1 M sodium hydroxide) decreased rapidly to about 1 mg kg^{-1} within 15 min and decreased reliably more to $0.2\sim 0.4 \text{ mg kg}^{-1}$ at 360~1,500 min. Thus, based on these results, alkaline extraction using sodium hydroxide is thought to be very effective in removing arsenic readsorbed in the surface of crystalline minerals at second washing

step. This is due to the ligand displacement reaction of hydroxyl ions with arsenic species and high pH conditions that can prevent readsorption of arsenic because predominant negatively charged crystalline oxides do not attract the negatively charged oxyanions.

Key words: soil washing, arsenic, sequential extraction