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# Chemical extraction of arsenic from contaminated soil under subcritical conditions

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ABSTRACT

In this research, we investigated a chemical extraction process, under subcritical conditions, for arsenic (As)-contaminated soil in the vicinity of an abandoned smelting plant in South Korea. The total concentration of As in soil was 75.5 mg/kg, 68% of which was As(+III). X-ray photoelectron spectroscopy analysis showed that the possible As(+III)-bearing compounds in the soil were $As_2O_3$ and R-AsOOH. At 20 °C, 100 mM of NaOH could extract 26% of the As from the soil samples. In contrast, 100 mM of ethylenediaminetetraacetic acid (EDTA) and citric acid showed less than 10% extraction efficiency. However, as the temperature increased to 250 and 300 °C, extraction efficiencies increased to 75–91% and 94–103%, respectively, regardless of the extraction reagent used. Control experiments with subcritical water at 300 °C showed complete extraction of As from the soil. Arsenic species in the solution extracted at 300 °C indicated that subcritical water oxidation may be involved in the dissolution of As(+III)-bearing minerals under given conditions. Our results suggest that subcritical water extraction/oxidation is a promising option for effective disposal of As-contaminated soil.

## 1. Introduction

Arsenic (As) is a well-known, toxic metalloid found in soils and natural waters. Arsenic can exist in various mineral forms in the natural environment. Among them, approximately 60% are arsenates, $As(+V)O_4^{3-}$, and the remaining 40% includes other forms, such as arsenite, $As(+III)O_3^{3-}$; arsenide, As(−III); sulfides; elemental As; and organic arsenic compounds (Alloway, 1994). Depending on the dosage and exposure time, As can cause acute and chronic toxicity in human beings, such as diarrhea, hypertension, vascular diseases, anemia, cancer, and leukemia (Alloway, 1994; Henke, 2009). According to Agency for Toxic Substances and Disease Registry (ATSDR, 2007), As was ranked no. 1 in the 2007 priority list of hazardous substances by Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). Because of the high toxicity and mobility, remediation of As-contaminated soils and groundwater has become an important issue in the last few decades.

Soil washing is an ex-situ treatment method for separating contaminants from soil via physical, chemical or physicochemical procedures (Evanko and Dzombak, 1997; Dermont et al., 2008a). Soil washing method mostly uses physical separation, such as size separation, gravity concentration, froth flotation, attrition scrubbing and magnetic separation (Dermont et al., 2008b; Dermont et al., 2010). Combined with chemical extraction, physical separation can also be used (Dermont et al., 2008a). In chemical extraction procedure, washing reagents may include leaching agents, surfactants, chelating agents, diluted acid/base solutions, and pH-adjusted water to enhance the removal of contaminants from the soil (Semer and Reddy, 1996; Peters, 1999; U.S. EPA, 2007; Dermont et al., 2008a). Soil washing has several advantages, including rapid kinetics, operational ease, treatability of fine particles, and economic efficiency (Dermont et al., 2008a; Peters, 1999). Due to these advantages, many efforts have been made worldwide over the past decades to apply soil washing in pilot facilities and full-scale demonstration facilities to remediate As-contaminated soil (Dermont et al., 2008a). In these facilities, the extraction efficiency of As from contaminated soil ranged from 6 to 95% (Legiec et al., 1997; Dermont et al., 2008a). As Peters (1999) concluded, the extraction efficiency of As in soil washing is strongly dependent upon the forms of the As in the soil.

Among the soil washing techniques, the chemical extraction methods were recently investigated for the removal of As from the contaminated soils using various washing reagents. Alam and Tokunaga (2006) showed that As was extracted most efficiently by 4% $H_3PO_4$ with more than 99% from the contaminated soil. Sulfuric acid and citric acid also showed high percentage of extraction efficiency. Though NaOH showed higher extraction efficiency, only arsenate (As(+V)) was extracted from the soil. Alam and Tokunaga (2006) also found that most of arsenite (As(+III)) was oxidized to arsenate during mineral acid and alkaline extraction. The extraction efficiency also varied with the concentration of the acid and alkaline solution. These results suggest that the pH and redox reactions may

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control the extraction of As from soil. Yang et al. (2009) showed that, compared to HCl, $H_3PO_4$, and $H_2SO_4$, NaOH was favorable in removing As from mine tailings. A combination of chelant extraction and iron reducing bacteria also increased the extraction efficiency of As from contaminates soils from 35% to 90% (Vaxevanidou et al., 2008). To date, several attempts have been made to remediate As-contaminated soils in South Korea via chemical extraction, and some successful results have been reported. Lee et al. (2004) showed, via batch experiments with 0.1 M ethylenediaminetetraacetic acid (EDTA), that more than 80% of the As could be removed from abandoned mine tailings and soils; they also showed that the extraction efficiency increased when the pH was less than five or more than ten. Jang et al. (2005) showed that alkaline washing with 0.2 M NaOH was more effective for removing As from mine tailings and soils than washing with citric acid. In contrast, Lee et al. (2007) used 0.2 M citric acid to wash stream sediments near an abandoned mine and reported that the removal efficiency of metals including As was greater than 95% after 1 h of washing. In bench-scale demonstration and field application of soil washing for As-contaminated soils (Korea Ministry of Environment, 2009a; Ko et al., 2005, 2006), it was also reported that, due to the limitation of chemical extraction, the physical separation of particles could enhance the overall efficiency of soil washing.

Subcritical water is liquid water under pressure at temperatures between the usual boiling point (100 °C) and the critical temperature (374.1 °C) (LaGrega et al., 2000). Under subcritical conditions, the dielectric constant, surface tension, and viscosity of water molecules are dramatically decreased (Siskin et al., 1990; Kuhlmann et al., 1994; LaGrega et al., 2000). Also, under subcritical conditions, concentrations of $H^+$ and $OH^-$ are greatly increased via self-ionization of water molecules (Kuhlmann et al., 1994). In addition, the combination of subcritical water with oxidizing agents, such as $H_2O_2$, permanganate, $O_2$, and air, can effectively oxidize organic compounds that are normally very difficult to oxidize (Kronholm et al., 2001; Dadkhah and Akgerman, 2002). Thus, over the last few decades, attempts have been made to utilize subcritical water to extract or decompose polycyclic aromatic hydrocarbons, pesticides, polychlorinated biphenyls (PCBs), dioxin, and other organic contaminants in soils (Hawthorne et al., 2000; Lagadec et al., 2000; Weber et al., 2002; Kubátová et al., 2002; Hashimoto et al., 2004). In contrast, only limited efforts have been made to use subcritical water to extract metals from contaminated soils (Priego-López and de Castro, 2002).

Currently, the Ministry of Environment of South Korea is planning to take action to remediate the Janghang area located in the southwestern Korean peninsula. The Janghang area is heavily contaminated with As and other metals, which were released from a Au–Cu smelting plant that was operated from 1936 to 1989 (Korean Environment Corporation (KEC), 2009). Previous investigations by the Ministry of Environment of South Korea have reported that areas within approximately 1.5–2.0 km from the abandoned smelting plant are contaminated with As. Similar to As distribution from other smelting plants (Helsen, 2005), it was reported that $SO_2$ and $As_2O_3$ were released from a stack and distributed to the soil through atmospheric dispersion (KEC, 2009). In order to select a remediation process, national research projects are being conducted to select optimal remediation technologies.

In this study, the chemical extraction of soil under subcritical conditions was investigated as one of the potential processes to treat As-contaminated soils in the Janghang area. It was hypothesized that the elevated temperatures and pressures associated with subcritical conditions would enhance the extraction of As due to the increased solubility of As compounds and the oxidation of As(+III)-bearing minerals under these conditions. Batch experiments at various temperatures with various types of washing reagents were performed to determine the optimal temperature to maximize the extraction of As from the soil.

## 2. Materials and methods

### 2.1. Chemicals

NaOH (98%, Dae Jung Chemical, Korea), citric acid (99.5%, Oriental Chemical, Korea), EDTA (99.5%, Yakuri Pure Chemical, Japan), $HNO_3$ (35%, DO Chemical, Korea), HCl (69–70%, Junsei Chemical, Japan), and acetic acid (99%, Dae Jung Chemical, Korea) were purchased and used as received.

### 2.2. Sampling and characterization of soils

As-contaminated soil was sampled from a location within 1 km of an abandoned smelting plant in the Janghang area. The sample was dried at room temperature out of the direct sunlight. The completely dried soil was crushed using a mortar and pestle and screened by a 2-mm sieve to remove any coarse particles. Particle size analysis was conducted using a laser particle size analyzer (Mastersizer 2000, Malvern, U.K.). Minerals in the soil were qualitatively identified via X-ray diffraction (XRD) analysis using an X-ray diffractometer (RAD-3C, Rigaku, Japan). X-ray photoelectron spectroscopy (XPS, Model K-Alpha, Thermo Scientific, Waltham, MA, USA) analysis was performed to qualitatively identify the As-containing forms in the soil. Loss on ignition was determined by weighing the sample before and after it was heated at 600 ± 25 °C for 3 h using a muffle furnace (Model 184A, Fisher Scientific, Pittsburgh, PA, USA). The pH of the soil was measured by an Accumet 925 pH/ion meter (Fisher Scientific, Pittsburgh, PA, USA) after 5 g of soil were mixed with 25 mL of deionized water and agitated for 1 h.

### 2.3. Elemental analysis and determination of chemical forms of As

Elemental analysis was conducted through an aqua regia extraction following a Korean standard method (Korea Ministry of Environment, 2009a). One milliliter of $HNO_3$ and 3 mL of HCl were added to a 0.25-g

**Table 1**
Sequential extraction method used to examine chemical fractionation of As. (Wenzel et al., 2001[a]).

| Arsenic analysis | | |
|---|---|---|
| Steps | Extractants | Conditions |
| I. Ionically bound soluble | 1 M $MgCl_2$ (pH 8), 25 mL | 2 h shaking, 25 °C |
| II. Adsorbed | 1 M $NaH_2PO_4$ (pH 5), 25 mL | 20 h shaking, 25 °C |
| III. Amorphous and poorly crystalline hydrous oxide of Fe and Al | 0.2 M $NH_4^+$-oxalate (PH 3.2), 25 mL | 4 h shaking, 25 °C |
| IV. Crystalline Fe oxyhydroxide | 0.5 M Na-citrate, 8 mL/1.0 M Na-bicarbonate, 8 mL/Na-dithionite, 0.4 g | 1) Add 8 mL of Na-citrate<br>2) Add 1 mL of Na-bicarbonate<br>3) Heat the tube in a water bath at 75–80 °C[b]<br>4) Add 0.2 g of Na-dithionite powder, stir for 5 min<br>5) Add a second 0.2 g of Na-dithionite powder, stir f or 10 min |
| V. Residual | Aqua regia ($HNO_3$ + HCl) | 1 h, 70 °C |

[a] Modified according to Kim et al. (2003), Ahn et al. (2005), and Keon et al. (2001).

[b] Do not over 80 °C.