

Arsenic contamination of soils and sediments from the tailings in the vicinity of Myungbong Au mine, Korea

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1. Introduction

Arsenic-bearing tailings piles, as a consequence of many gold-mining operations, can be an important source of environmental contamination. Myungbong mine is located in the Boseong-gun, Jeollanam-do, and was actively operated in the early 1900s. Until the 1970s, it was mined intermittently, and 5,500 m³ of mine dumps were deposited during operation. In a preliminary study, Myungbong mine is highly arsenic-affected area accompanying only low heavy metal contamination. Objectives of the study are (1) to probe the source and the geochemical retention of As released from the tailings dump with a high As concentration, and (2) to reveal the pathway of contamination into agricultural area.

2. Materials and method

Samples of tailings, soils, and sediments were taken at the mine site, nearby pond, and agricultural field. Total contents of major elements and trace elements (As, Cd, Cu, Pb, and Cr) were analyzed by X-ray fluorescence and ICP-AES (Thermo Jarrel Ash), respectively. Water samples were collected at the nearest pond, stream, and domestic wells in the study area. Dissolved As and heavy metals were analyzed by ICP-MS (VG/PQ2turbo). A sequential extraction method, originally suggested by Woolson et al. (1973), was applied to solid samples to separate operationally defined As-binding phases. Undisturbed subsamples were embedded in epoxy resin, and polished thin sections prepared for Electron Probe Micro-Analysis (EPMA, JEOL/JXA8900R). Mineral identification in solid samples was conducted by X-Ray Diffraction (XRD) using a Rigaku X-ray generator.

3. Results and discussion

3.1. Mineralogy

Several grains from surface and subsurface tailing samples were selected for EPMA analysis using WDS (Wavelength Dispersive Spectrometer). The primary sulfide mineral is predominantly pyrite, and has been almost completely dissolved or oxidized. The secondary product of weathered pyrite remains as

a noncrystalline Fe-oxyhydroxide. These were identified in XRD pattern of amorphous compounds collected around the residual pyrite. In pyrite, As is present as a solid solution, and the altered pyrite grains are partially dissolved. In BSE (Backscattered Electron) images, the bright core represents remnant of pyrite, and the dark thin rim is Fe-oxyhydroxide, which are formed from oxidation of pyrite. Pyrite grains distinctly show a concentric zoning pattern. This indicates arsenic have been leached out, leaving Fe-rich core. Consequently, oxyanionic sorption reaction of As is involved in Fe-oxyhydroxide formed from pyrite. Because pyrite is progressively oxidized, Fe-oxyhydroxide becomes the main sorbent adsorbing As around pyrite. Positive correlations between As and oxalate-extractable Fe in mine tailings suggest that As is adsorbed onto the Fe-oxyhydroxide. However, negative correlations between As and total Fe suggest that pyrite broke down during oxidation (Boulet & Larocque 1998). Oxalate selectively dissolves noncrystalline and poorly crystalline Fe-related mineralogical forms, whereas total Fe concentration includes all phases including sulfide minerals. This implies that tailings dump has undergone a progressive weathering process, and the mineralogical forms have been changed into short-range order phases such as Fe-oxyhydroxide. The short-range order phases may strongly adsorb toxic elements leached from primary phases.

3.2. Geochemistry of tailings, soils, and sediments

Concentrations of heavy metals are relatively low in tailings and pond sediments, but As content is measured as 2770 mg/kg in average. The trend of metal concentrations is symmetric for particle size distribution in the slightly oxidized tailings, but is asymmetric in the highly oxidized tailings. The asymmetric pattern in the highly oxidized tailings shows that As and heavy metals are enriched in smaller particle size fraction. In particular, concentrations of As, Pb and Cu are concentrated in fine fraction. It is suggested that fine secondary minerals may be formed from dissolution of primary sulfides and the elements are associated with this fraction. But the concentration of Cd shows slightly decreasing plateau pattern because Cd is more soluble and easily transported into groundwater than other metals. High metal concentration in large grain fraction implies that large mineral grains and Fe-coated particles control metal release.

Total As (mg/kg):	2769	1887	91.9	113	204	142	263	506
Number of sample:	N=6	N=6	N=3	N=2	N=2	N=2	N=4	N=1

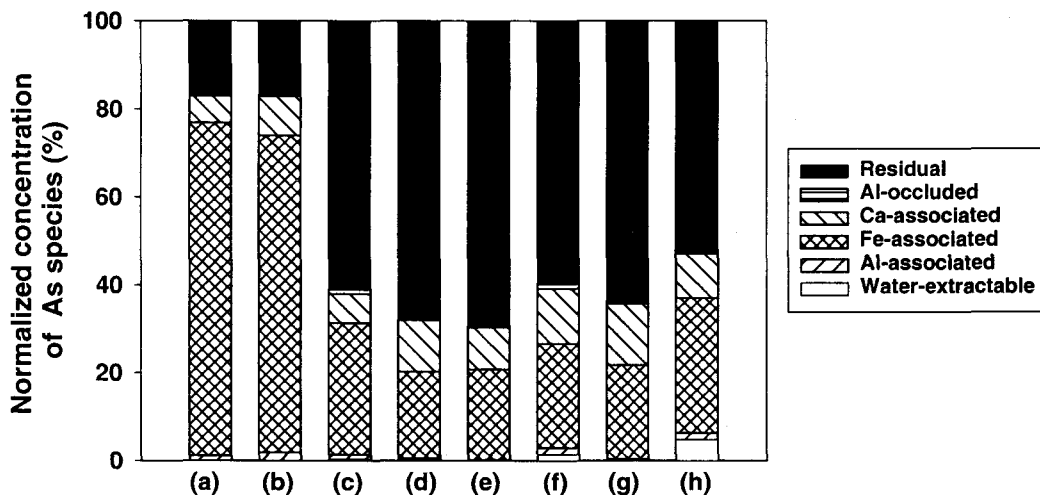


Figure 1. As speciation in (a) surface tailings, (b) subsurface tailings, (c) paddy soil, (d) farmland soil, (e) an upper layer and (f) a lower layer in small pond sediment, (g) bulk sediment samples in small pond, and (h) bulk sediment samples in large pond.

In an oxyanionic sequential extraction, non-residual fraction of As is separated into five forms with water soluble, Al-associated, Fe-associated, Ca-associated, and Al-occluded forms (Tiessen & Moir, 1993). Arsenic in this study area tends to be associated with the Fe-, Ca-, Al-associated and residual fractions in order (Fig. 1). Most labile As fraction accounts for <5% of total As. Although substantial difference depending on sites and depths is present, the retention of As is constrained by low arsenate solubility in Fe-associated fraction. Tailings have undergone oxidation, and Fe-associated fraction increases from transformation of pyrite into Fe-oxyhydroxide. In the pond sediment, the large pond sediments have a higher concentration of water-soluble As than small pond sediments, because a decrease of redox potential in sediment increases the amount of dissolved Al and Fe from the crystalline phases (McGeehan et al.1998). This indicates that pond sediments and tailings have high potential of As release, and bioavailability and mobility of As in sediments and tailings are greater than those in the agricultural soils.

3.3. Water chemistry

Stream and pond water samples next to tailings dump have neutral to slightly alkaline pH values (6.50 to 8.10). Under this pH condition, heavy metals can be stable forms and their transport to surface water and groundwater is limited. However, As can have higher solubility, and is mobilized as various anionic forms. In stream waters of the study area, dissolved metal concentrations were significantly low, but As was enriched to 80.1 ppb. Irrigation water and well water samples also contain As exceeding the level of WHO guideline, 10ppb. Farmland and paddy fields of the study area have been irrigated from the stream contaminated with As. Although direct input of mine tailings to agricultural field by erosion is less expected, poor quality of irrigation water can have a potential impact on growing crops and residents through a chemical transport of As from tailings.

4. Reference

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