# Assessment of pilot-scale acid washing of soil contaminated with As, Zn and Ni using the BCR three-step sequential extraction

Ilwon Ko [a,*], Yoon-Young Chang [b], Cheol-Hyo Lee [a], Kyoung-Woong Kim [c]

[a] *Environmental Research Center, OIKOS Co. Ltd., Daeryung Techno Town Building, 8-Cha, 481-11, Room 1007, Gasan-dong, Geumcheon-gu, Seoul 153-775, Korea*
[b] *Department of Environmental Engineering, Kwangwoon University, 447-1, Wolgye-dong, Nowon-gu, Seoul 139-701, Korea*
[c] *Arsenic Geoenvironment National Research Lab (NRL), Department of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), 1, Oryong-dong, Buk-gu, Gwangju 500-712, Korea*

## Abstract

This study performed pilot-scale washing of soil contaminated with both oxyanion and cations as a recalcitrant remediation case due to their different chemical behavior. The soil contaminated with As, Zn and Ni, partially recalcitrant due to their strong binding properties, was obtained near a closed iron/serpentine mining area. This study monitored the variation of chemical speciation of As, Zn and Ni for acid solutions and particle size fraction using the BCR sequential extraction and evaluated the optimal condition of physical separation of highly contaminated fine particles for enhanced washing. $H_2SO_4$ and $H_3PO_4$, including competitive oxyanions, enhanced removal of As with the simultaneous extraction of Zn and Ni. Less nickel from the residual fraction in coarse particles was extracted than As and Zn due to the recalcitrant serpentine. Fe/Mn oxide, organic/sulfides and residual fractions in fine particles were enriched with contaminants due to the high surface areas and recalcitrant minerals. The chemical extraction of As was also restricted in the fine particles, whereas the chemical extraction of Zn and Ni was determined by the residual form of various particle size fractions. Further extraction was limited in the exchangeable and residual fractions and retained a gradual extraction from Fe/Mn oxide and organic/sulfides fractions, which indicated an instant detachment from the easily bound fraction. Correspondingly, extraction from the acid-attackable fraction was related to the exchangeable Fe/Mn oxide and organic/sulfides fractions. Due to the limitation of chemical extraction, the physical separation of fine particles could enhance the effectiveness of acid washing. In addition, the chemical properties of the soil were affected by strong acid washing. The treated soil then needed to be regenerated.

## 1. Introduction

Contamination by As (arsenic) and heavy metals is problematic in the geochemical environment around metal mining areas due to arsenic-related chemical spills in agricultural and industrial areas [1,2]. Arsenic and heavy metals have been also contaminants in metallic ores and industrial effluents in Korea [3–6]. Exposure to arsenic and some metals carries risks for humans, such as cancer. The remediation of soil contaminated with As and heavy metals is an important problem for many countries [2]. Soil contaminated with As and heavy metals have been physically, chemically and biologically treated. Physical methods include separation, carbon adsorption, vitrification and incineration. Chemical methods such as solidification/stabilization, encapsulation and washing remove metals or immobilize them by reducing bioavailability. Biological methods use plants or microbes for the removal of metals. The simultaneous removal of As and heavy metals is strongly dependent on chemical speciation with respect to the redox potential and pH [1,7]. Specifically, the solubility of most cationic metals decreases as the solu-

* Corresponding author. Tel.: +82 2 855 5166; fax: +82 2 855 6451.
*E-mail address:* iwkoh@hanmail.net (I. Ko).

tion pH increases. However, the solubility of oxyanions such as As, Se, P and Mo increases as pH increases [8]. It is not easy for both oxyanion and cation to find optimal conditions for leaching or immobilization.

Soil washing technology has been applied to the decontamination of heavy metal-contaminated soil such as EDTA and DTPA extraction of Zn [9], EDTA extraction of Pb [10,11] and acid washing of heavy metals [12]. Soil washing of As has been also treated with sodium hydroxide extraction in an alkaline environment [13], phosphate extraction [14] and acid washing [15]. There have been only a few cases described about the simultaneous removal of As and heavy metals. For the simultaneous removal of As and heavy metals, an optimal remedial condition should be set up. This study provides an example of an optimal site-specific study. Two predominant operating factors in soil washing are the chemical extraction of contaminants and the physical size separation of fine particles. Soil remediation is a site-specific process, and, in particular, the chemical speciation of As and heavy metals should be significantly monitored for optimal extraction due to the nature of their binding strengths. Chemical fraction of metals with weak bonding strength can be mobilized and available for uptake. However, metals that have bonded strongly with soil minerals are less exchangeable. It is important to understand the chemical forms of metals for remedial work. Many researchers have suggested modified sequential extraction schemes for selective leaching of particular chemical forms of elements from sediment, soil or waste [6,16–19]. Further, sequential extraction can assess the effectiveness of the remedial processes such as electrokinetic removal of heavy metals [20,21], the application of till cover of mine tailings [22] and the stabilization of As [23]. Particularly, a group in a Community Bureau of Reference (BCR) project proposed a three-step extraction procedure [18,24]. The BCR scheme is now widely used in the analysis of sediment, soil, sludge and mine waste. Therefore, the BCR method can be applied to monitor chemical forms of metals during soil washing in order to evaluate the proper extraction efficiency of contaminants. The physical size separation, a factor that affects enhanced soil washing, can control the levels of contaminants in the treated soil. The fine particles have a high surface area for the adsorption of contaminants; therefore, the concentrations of contaminants are extremely high. However, the extraction of metals in the fine particles is very poor, less movable and available for uptake in the ecosystem. If the fine particles are properly separated, the overall effectiveness of soil washing is enhanced.

In this study, the pilot-scale washing of soil contaminated with both As and heavy metals was performed as a recalcitrant case. The objectives of this study are to find the optimal conditions of pilot-scale acid washing for the simultaneous removal of As and heavy metals and to evaluate the characteristics of soil contaminants using the sequential extraction method during soil washing. Specifically, we characterized the soil properties for soil washing in the contaminated area, the effect of the acid solution type and the effect of the reaction time for acid washing. Then, we monitored the variation of chemical fractions of As, Zn and Ni with respect to both the acid solutions and particle sizes during the acid washing, and determined the optimal size for physical separation of fine particles as a residual form of contaminant.

## 2. Materials and methods

### 2.1. Site description and sampling

The Dalcheon iron mining area is located in the southeastern part of Seoul, Korea, approximately 450 km (Fig. 1). The study area will be a hilly district on a plain with a res-
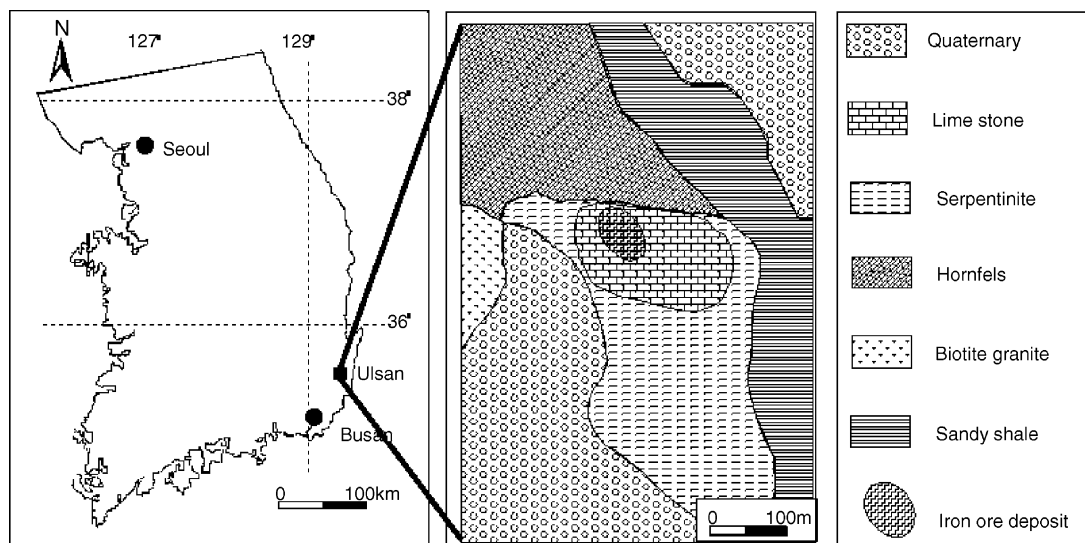


Fig. 1. Study site and geological map.

ident apartment complex. The Dalcheon iron mine has been exploited and yielded manly iron from 1906 to 1993 and partially serpentine rock from 1966 till quite recently. Historically, the iron mining activities has frequently lasted for about 1700 years [25]. The geological setting of this area is also shown in Fig. 1. Main rock formation is consisted of granite, shale, limestone and serpentine rock [26]. Lime stone is overlain by serpentine rock, granite and metasedimentary rocks. Pyrite-rich sulfide ore bodies are intercalated within a limestone unit as a hydrothermal alteration skarn-type. The serpentine and magnetite were ore minerals in the rock formation. The serpentine is enriched in Ni and magnetite is a contamination source of As including arsenopyrite and As-bearing pyrite. The basement of limestone can be attributed to prevent the sulfide oxidation from producing acid mine drainage. The mine tailings have been deposited in an above ground of mining site and enriched in As, Zn and Ni, and serpentine rock including dominantly Ni has been also piled in that area. Then nearby natural soils are contact with tailings and serpentine rock. The contaminated area near the iron mine was designed to remediate the contaminated soils with the soil washing technology of contaminated soils. The impoundment of mine waste such as tailing and waste rock was designed to be remediated by the application of till cover after stabilization. The annual precipitation in this area is 1480 mm/year and the mean temperature is 17 °C [27].

The bulk soil was sampled and blended with an excavator, and removed gravel by screening. Bulk samples chosen were naturally dried at 50 °C and sieved. The soil particles of less than 10 mm of contaminated soils were used for soil washing in order to give the comparable results of the pilot-scale experiments of soil washing. The coarser particles such as gravel were in general identified as non-contaminated fraction on the contrary to the primary minerals and secondary weathered fine fractions including contaminants.

## 2.2. Pilot-scale soil washing experiment

The pilot-scale soil washing equipment used in this study consisted of five principle parts; soil washing scrubber (drum-type), vibrating screen, screw feeder, high-pressure air supply and ceramic filter system as shown in Fig. 2. The screw feeder was able to transfer contaminated soil into the washing scrubber simultaneously mixing washing solution with soil:solution ratio of 1:10. The washing scrubber has a drum-type cylinder with the inner screw blade to help soils move forward. While being treated, treated soils and washing solution were shaken with strong mechanical turbulence by the high-pressure air supply. The compartment extracted contaminants by enhancing contact surface area for the extraction reaction and reducing soil particle size. The rotating velocity of washing scrubber can be controlled by rpm (revolutions per minute). Moreover, after treated soils and washing solution pass through the washing scrubber, they are separated and screened by the vibrating screen with 200 mesh (0.074 mm) sieving size. In the ceramic filter system, the waste wash-

ing solution was treated with settling the fine particles and adsorbing dissolved inorganics and recycled for new washing solution with the addition of acid solution. All parts of the soil washing equipment were made of stainless steel.

The soil of each batch, 40 kg, was put into the screw feeder for 5 min and the acid solution for washing was also transported together with 1:10 of soil:solution ratio. HCl, $H_2SO_4$ and $H_3PO_4$ were used for the acid washing of contaminated soil. For the effective extraction, the washing solution was kept with pH 2–3. During the experiment, the changes in solution pH were monitored in the front and end compartment of washing scrubber. After each batch of treated soils was carried out, mean pH was obtained from five-time measurements in the front and end compartment. In addition, water-washing as a control was also tested in the same way. In order to investigate the effect of the reaction time on the acid-washing for the optimal extraction of contaminants, it was varied by controlling the rpm of washing scrubber. The reaction time was calculated from the recovery of more than 80% of total input soil, considering the loss of fine soil particles. The remediated soils were sampled and weighed at each time interval of 4, 7, 10, 13, 16, 19, 22, 25 and 28 min for the cumulative weight of soils. The acid-washed soil was screened in the vibrating screen and then soil particles of more than 0.074 mm (>200 mesh) were discharged out as a remediated soil. The remediated soils were sampled every batch and instantly sieved into five fractions (0.074–0.149, 0.149–0.250, 0.250–0.420, 0.420–0.841 and 0.841–10 mm). Both bulk and five-fraction soil were extracted with aqua regia (HCl:$HNO_3$ = 3:1) and the BCR sequential extraction method for As, Zn and Ni, and then all solutions were stored at 4 °C for the analysis.

For monitoring the change of washing solution, washing water was also sampled at drain of vibrating screen (Fig. 2) and stored for a chemical analysis following the instant filtration through 0.45 μm filter and acidification with nitric acid (1 M). The contaminants (As, Zn and Ni) and major elements (Al, Fe, Mn, Mg, Ca, Na and Si) were selected.

## 2.3. BCR three-step sequential extraction procedure

The BCR three-step sequential extraction procedure was developed by Quevauviller et al. [24] and slightly modified [18,28]. In step 1 of the extraction in 0.11 mol L$^{-1}$ acetic acid at pH 2.8, metals present in ionic form, bound to carbonates and the exchangeable fraction were released. In step 2 of the extraction in 0.1 mol L$^{-1}$ hydroxylamine hydrochloride at pH 2, metals bound to amorphous Fe and Mn (hydro)oxides were leached. In step 3 of the oxidation in acid-stabilized 30% hydrogen peroxide and extraction in 1 mol L$^{-1}$ ammonium acetate at pH 2 adjusted with nitric acid, metals bound to organic matter and sulfides were separated. For an internal check on the sequential extraction procedure, the residual from step 3 was digested in hydrochloric acid and nitric acid of 3:1 ratio (aqua regia) (step 4). The concentrations of metals in step 1–4 were summed and compared with their

Soil: Solution= 1:10
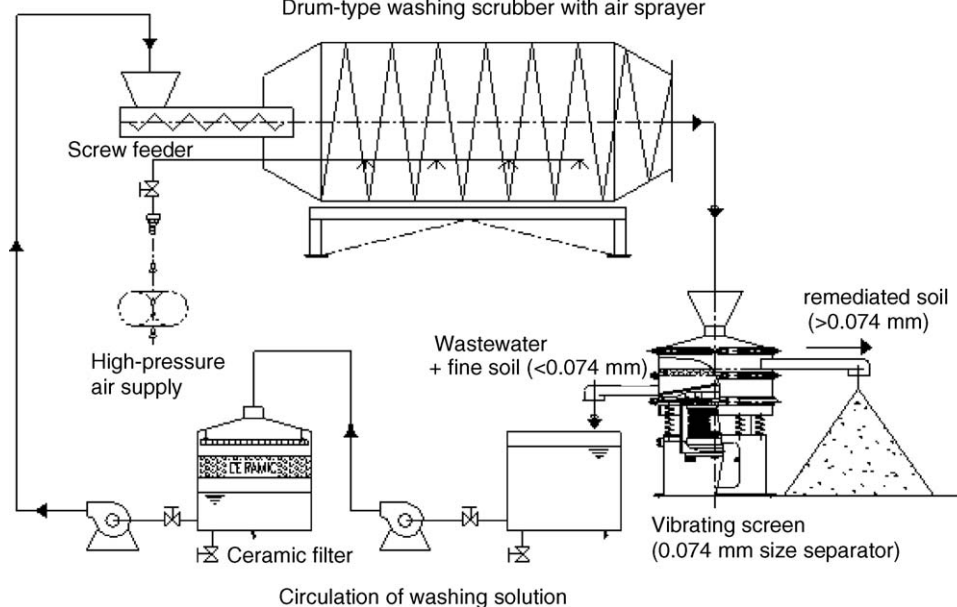Drum-type washing scrubber with air sprayer

Fig. 2. Schematic diagram of pilot-scale soil washing process.

total concentration of the original sample. In each analytical step, standard and blank samples were also analyzed, and duplicate samples were prepared. Results of extraction steps were expressed on a dry mass basis. Reagents were prepared according to the procedures described by Quevauviller et al. [24].

### 2.4. Analytical methods

The total metal concentrations of original and acid-washing samples were determined in duplicates after hydrochloric acid and nitric acid of 3:1 ratio (aqua regia). Zn and Ni were determined by induced coupled plasma atomic emission spectrometry (ICP-AES, Thermo Jarrel Ash) under the optimal measurement conditions. The level of total dissolved As were determined by hydride generator-atomic absorption spectrometry (HG-AAS, Perkin-Elmer ZL 5100). The quantization limits of HG-AAS were $1.0 \, \mu g \, L^{-1}$ As and

$24 \, \mu g \, L^{-1}$ As. The analysis method was followed by the standard methods of water and wastewater [29]. The sodium borohydride (Sigma–Aldrich Chem Co.) solution was supplemented with 0.1 M sodium hydroxide and 10 wt.% HCl solution (Merck) was used for carrier.

Soil particle analysis was performed by sieving and weighing the air-dried soil with five fraction (0.074–0.149, 0.149–0.250, 0.250–0.420, 0.420–0.841 and 0.841–10 mm). Potentiometric titration with a micro-titrator (702SM, Metrohm) was performed to measure the acidity of 1.0 g soil with 1.0 M HCl under $N_2$ gas purging to prevent carbonate effects. The deionized water was also titrated in order to calculate the acidity of soil from their difference. The soil pH was determined by weighing 10 g of air-dried and sieved (<10 mm) soil into a beaker and adding 100 mL deionized water and stirring for 30 min. The pH values of the samples were determined using an Orion ion analyzer (Orion Research Inc.) equipped with a pH electrode. The content

Table 1
Chemical speciation of bulk contaminated soils

| Analysis | Fraction | Concentration (mg kg$^{-1}$) | | |
|---|---|---|---|---|
| | | As[a] | Zn | Ni |
| BCR sequential extraction | Exchangeable | $0.9 \pm 0.1$ | $46 \pm 3.8$ | $2.4 \pm 0.3$ |
| | Fe/Mn (hydro)oxides | $8.9 \pm 0.3$ | $103 \pm 5.2$ | $23 \pm 3.3$ |
| | Organic/sulfides | $2.0 \pm 0.3$ | $43 \pm 4.4$ | $5.2 \pm 0.4$ |
| | Residual | $40 \pm 2.5$ | $216 \pm 12.5$ | $71 \pm 4.7$ |
| | Sum | 52 | 408 | 102 |
| Aqua regia extraction (HCl:HNO$_3$ = 3:1) | | 41 | 335 | 88 |

[a] Values represents the mean and standard deviation of five soil samples.

Table 2
Removal efficiencies of As, Zn and Ni calculated by the acid-extraction

| Particle size (mm) | Particle size fraction of untreated soil | Untreated soil concentration (mg kg$^{-1}$) | | |
|---|---|---|---|---|
| | | As | Zn | Ni |
| < 0.074 | 0.02 | 66 | 513 | 73 |
| 0.074–0.149 | 0.05 | 59 | 451 | 70 |
| 0.149–0.25 | 0.10 | 48 | 423 | 56 |
| 0.25–0.42 | 0.19 | 43 | 371 | 69 |
| 0.42–0.841 | 0.09 | 35 | 346 | 70 |
| 0.841–10 | 0.54 | 29 | 285 | 75 |
| Total | 1.00 | 37 | 334 | 71 |

| Particle size (mm) | Particle size fraction of treated soil | HCl washed soil concentration (mg kg$^{-1}$) | | | HCl washing efficiency (%)[a] | | |
|---|---|---|---|---|---|---|---|
| | | As | Zn | Ni | As | Zn | Ni |
| < 0.074 | – | | | | | | |
| 0.074–0.149 | 0.05 | 68 | 551 | 157 | 63 | 59 | 38 |
| 0.149–0.25 | 0.12 | 47 | 267 | 78 | 72 | 67 | 49 |
| 0.25–0.42 | 0.21 | 10 | 149 | 68 | 87 | 76 | 62 |
| 0.42–0.841 | 0.08 | 5.3 | 153 | 22 | 93 | 86 | 82 |
| 0.841–10 | 0.51 | 3.8 | 69 | 21 | 100 | 100 | 100 |
| Total | 0.97[b] | 14 (63%) | 138 (59%) | 44 (38%)[c] | | | |

| Particle size (mm) | Particle size fraction of treated soil | H$_2$SO$_4$ washed soil concentration (mg kg$^{-1}$) | | | H$_2$SO$_4$ washing efficiency (%) | | |
|---|---|---|---|---|---|---|---|
| | | As | Zn | Ni | As | Zn | Ni |
| < 0.074 | – | | | | | | |
| 0.074–0.149 | 0.06 | 72 | 537 | 149 | 70 | 58 | 42 |
| 0.149–0.25 | 0.12 | 27 | 322 | 87 | 82 | 67 | 54 |
| 0.25–0.42 | 0.18 | 6.5 | 152 | 70 | 91 | 79 | 69 |
| 0.42–0.841 | 0.10 | 5.8 | 154 | 26 | 94 | 87 | 87 |
| 0.841–10 | 0.51 | 3.5 | 53 | 13 | 100 | 100 | 100 |
| Total | 0.97[b] | 11 (70%) | 141 (58%) | 41 (42%) | | | |

| Particle size (mm) | Particle size fraction of treated soil | H$_3$PO$_4$ washed soil concentration (mg kg$^{-1}$) | | | H$_3$PO$_4$ washing efficiency (%) | | |
|---|---|---|---|---|---|---|---|
| | | As | Zn | Ni | As | Zn | Ni |
| < 0.074 | – | | | | | | |
| 0.074–0.149 | 0.05 | 46 | 516 | 137 | 75 | 61 | 45 |
| 0.149–0.25 | 0.13 | 30 | 319 | 76 | 82 | 68 | 54 |
| 0.25–0.42 | 0.20 | 6.4 | 143 | 74 | 93 | 81 | 69 |
| 0.42–0.841 | 0.07 | 5.9 | 142 | 21 | 96 | 89 | 89 |
| 0.841–10 | 0.52 | 2.2 | 51 | 11 | 100 | 100 | 100 |
| Total | 0.97 | 9 (75%) | 132 (61%) | 39 (45%) | | | |

[a] The efficiency is calculated from the concentrations of residual particles after the removal of above-sized fine particles.

[b] The wt.% of the treated soil was adjusted to account for the loss of 3% of the fine soil (<0.074 mm).

[c] The values in parenthesis represents the removal efficiency based on the variation of concentration with respect to all particle size fractions.

of organic matter in soil was gravimetrically determined by 450 °C-ignition at oven. Mineral identification in the solid samples was performed by X-ray diffraction (XRD) using a Rigaku X-ray diffractometer with a Cu tube.

## 3. Results and discussion

### 3.1. Characterization of contaminated soil

The particle size analysis of the contaminated soil consisted of sand (97.4%) and silt and clay (2.6%), which represented the textural classification of sandy soil. The sandy soil was suitable for applying soil washing [30,31]. Because the soil washing equipment in this study screened out fine soil particles of less than 0.074 mm with a 200 mesh sieving screen (Fig. 2), the fine particles were expected to yield sludge of at least 2.6% of the total bulk soil due to their highly recalcitrant contamination. The XRD analyses of the contaminated soil show kaolinite, feldspar, quartz, magnetite, hematite, serpentine and pyrite, and, in particular, calcite. Ore minerals such as magnetite and serpentine were also observed; it is possible that a contaminated source mineral such as pyrite was present in the contaminated soil. The bulk soil was an alkaline soil of mean pH 7.6 (6.7–8.5), and con-

sumed $5.52 \times 10^{-1}$ mol H$^+$ kg$^{-1}$ with acid buffering due to the carbonate contents of the bulk soil.

The total concentration of As, Zn and Ni was found to be 41, 335 and 88 mg/kg ($n = 5$), respectively, and existed mainly in the residual fraction (Table 1). This means that the sulfides or silicate-associated As and Zn were incompletely extracted, and Zn was strongly incorporated into the serpentine as a dominant form of silicate mineral. Three contaminants were secondly enriched in Fe/Mn (hydro)oxides fraction. Arsenic and Zn in the untreated soil were enriched in fine particles, but Ni existed in both fine and coarse particles (Table 2). The enrichment of the contaminants can be explained due to the weathering of the primary minerals and the production of secondary weathered minerals [32]. Although the weathered minerals such as amorphous iron-(hydro)oxides or the secondary weathered minerals were not resolved in the XRD analysis, the presence of sulfide minerals from the bulk soil is expected to produce weathered minerals due to the oxidative weathering of sulfide minerals. However, the serpentine as a silicate mineral is recalcitrant to the weathering relative to the oxidation of sulfide minerals, and the Ni concentration seems to be enriched in both fine and coarse particle sizes.

Figs. 3–5 also show the chemical fractions of As, Zn and Ni in the untreated soil with respect to the particle sizes (<0.074, 0.250–0.420 and 0.841–2 mm), respectively (gray-
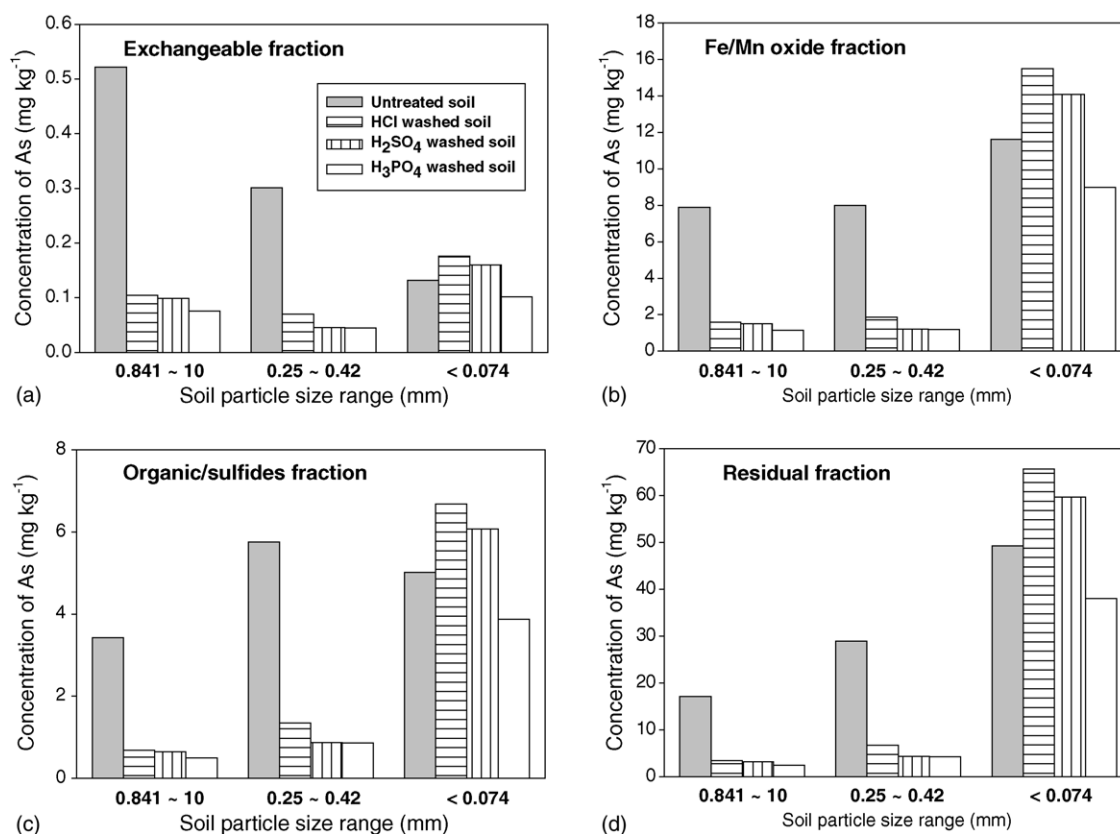


Fig. 3. Chemical fraction of As of the contaminated soil with respect to selected acid solution and soil particle size fractions (0.841–2, 0.420–0.250 and <0.074 mm): (a) exchangeable fraction, (b) Fe/Mn oxide fraction, (c) organic/sulfides fraction and (d) residual fraction analyzed by BCR sequential extraction method.
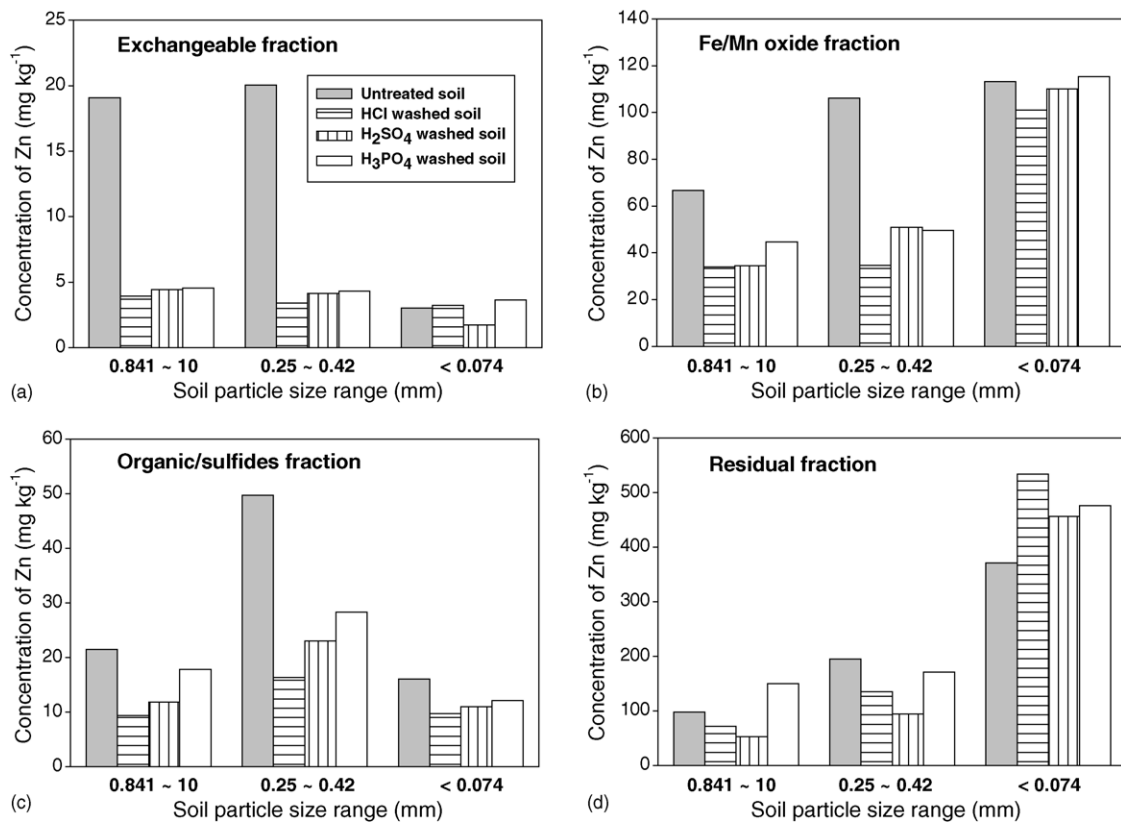
Fig. 4. Chemical fraction of Zn of the contaminated soil with respect to selected acid solution and soil particle size fractions (0.841–2, 0.420–0.250 and <0.074 mm): (a) exchangeable fraction, (b) Fe/Mn oxide fraction, (c) organic/sulfides fraction and (d) residual fraction analyzed by BCR sequential extraction method.

colored column). The exchangeable fractions of each metal were enriched in the larger particle size, but the residual fraction in finer particle size. The concentrations of As and Zn in the Fe/Mn oxide fraction increased in line with a decrease in soil particle size (Figs. 3b and 4b). The concentration of Ni in the Fe/Mn oxide fraction decreased (Fig. 5b), and the concentrations in the residual fraction (Fig. 5d) slightly increased (Table 2). Contaminants in the organic/sulfides fraction were enriched in the intermediate size fraction (Figs. 3c, 4c and 5c).

### 3.2. Operation factors of soil washing

For pilot-scale soil washing, the solution pH before and after the acid washing of contaminated soil was monitored, and the reaction time was controlled. The pH of the acid solution was measured in the influent and effluent of the washing scrubber (Fig. 2). The water washing of contaminated soil enhanced the pH of the effluent solution to pH 6.7, which was consistent with a neutral-to-alkaline soil pH of contaminated soil (Fig. 6a). In order to consistently adjust the reaction pH 2–3, the washing solution including 0.25 L for HCl, 0.125 L for $H_2SO_4$ or 0.083 L for $H_3PO_4$ circulated into the washing scrubber with 40 kg of soil based on the consumption of $5.52 \times 10^{-1}$ mol $H^+$ $kg^{-1}$ with the acid buffering of the bulk soil. The pHs in the influent and effluent solutions were maintained at pH 2–3 and 3–4, respectively (Fig. 6a).

The reaction time in the washing scrubber was determined by recovering treated soil. The vibrating screening physically separated the fine soil particles less than 0.074 mm. The rpms of the washing scrubber were controlled to the extent of 4, 2 and 1 rpm, and then produced 10, 13 and 25 min as reaction times of treated soil, respectively (Fig. 6b). The treated soil was recovered with a mean 83% (total dry wt.%/%) and a range of 81–87%. The soil was expected to be removed with the physical separation of <0.074 mm and remain in the washing scrubber because the fine particles need the longer reaction time due to the strong attachment to the inner parts.

### 3.3. Effect of acid solution

In order to evaluate the simultaneous removal effectiveness of oxyanionic As and cationic Zn and Ni, acid washing was performed. Although soil washing for the extraction of As can be properly performed in an alkaline condition, the solubility of cationic metals such as Zn and Ni is too low to dissolve in an aqueous solution [8,32,33]. In this study, HCl, $H_2SO_4$ and $H_3PO_4$ were used for acid washing. Moreover, because an alkaline extractant or solution including competing oxyanions such as phosphate and sulfate is effective in As removal [13–15], acid washing of cationic metals can be enhanced simultaneously with oxyanionic As. The inorganic contaminants are also incorporated into the recalcitrant min-
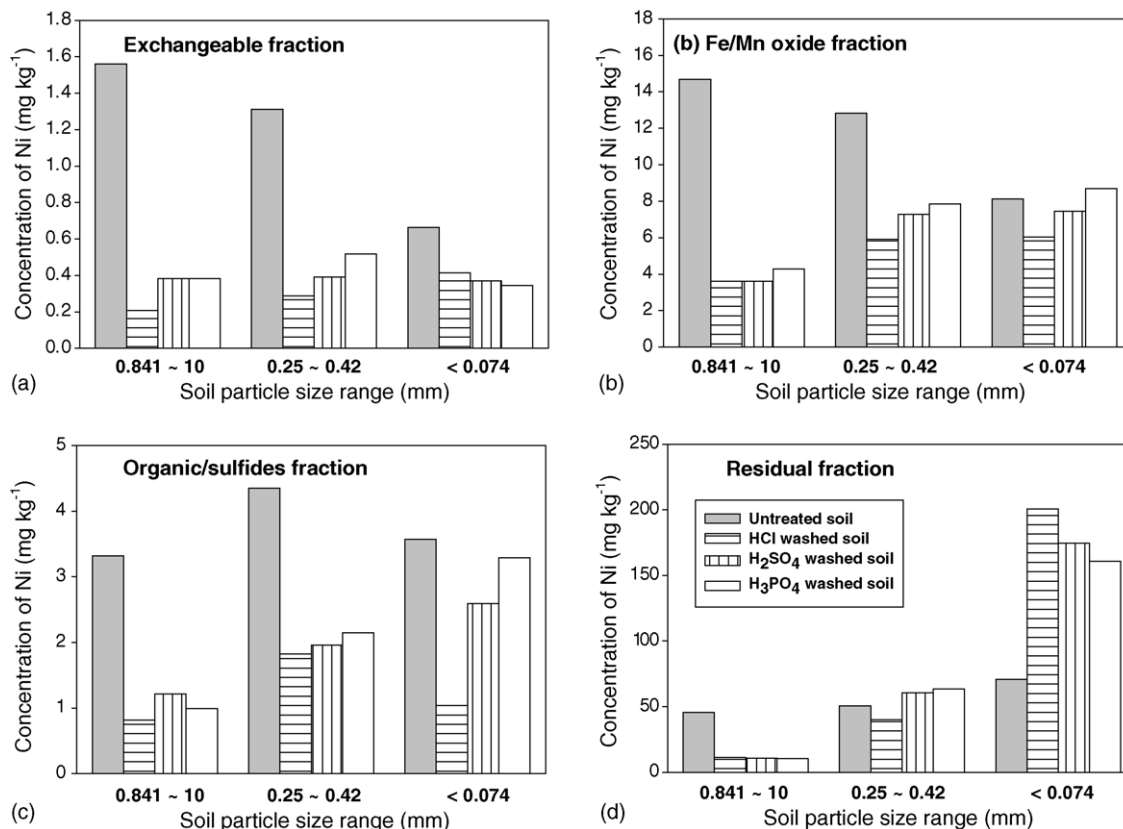
Fig. 5. Chemical fraction of Ni of the contaminated soil with respect to selected acid solution and soil particle size fractions (0.841–2, 0.420–0.250 and <0.074 mm): (a) exchangeable fraction, (b) Fe/Mn oxide fraction, (c) organic/sulfides fraction and (d) residual fraction analyzed by BCR sequential extraction method.

eral lattice or form strong bonds with mineral surfaces; the strong bonds may be broken effectively by the acid attack. Therefore, acid washing is expected to be a favorable treatment for the removal of both As and cationic metals.

The variation of As, Zn and Ni concentrations was investigated on the basis of soil particle size after the pilot-scale acid washing, as shown in Table 2. The adjusted concentrations of As, Zn and Ni were calculated from each mass ratio of particle size distribution and each concentration (Eq. (1))

$$C_j = \sum_i m_i C_i = m_1 C_1 + m_2 C_2 + \cdots + m_i C_i \qquad (1)$$

where $C_j$ is the adjusted concentration of the contaminant, $C_i$ is the measured concentration from each soil particle fraction and $m_i$ is the mass ratio of each soil particle fraction. The removal efficiency can be obtained by dividing the adjusted concentrations with the initial bulk concentrations (Eq. (2))

$$\text{removal efficiency} = \frac{C_j^i - C_j^t}{C_j^i} \times 100\,(\%) \qquad (2)$$

where $C_j^i$ and $C_j^t$ are the adjusted concentrations of the initial bulk soil and treated soil, respectively. The removal efficiency of As was higher for the $H_3PO_4$- and $H_2SO_4$-washing than that for the HCl-washing. This means that As was favorably

inhibited to be adsorbed or complexed onto/with soil minerals due to the presence of competing oxyanions [13]. However, the extraction of Zn and Ni was similar to the use of HCl, $H_2SO_4$ and $H_3PO_4$. Particularly, Ni was incorporated into the serpentine mineral; the removal efficiencies were very low. Therefore, the acid-extraction of Ni was inhibited due to the recalcitrant property of a silicate mineral in the contaminated soil. The acid solution that includes competitive oxyanions was favorable for soil washing of simultaneous contaminants of both oxyanionic As and cationic Zn and Ni.

### 3.4. Effect of soil particle size

Acid washing of coarse particles effectively removed As, Zn and Ni with a significant decrease in their concentrations (Figs. 3–5). High-removal efficiencies in coarse particles were performed particularly in As, Zn and Ni. Less nickel was extracted than As and Zn from the residual fraction in the coarse particles. This is also consistent with the recalcitrant incorporation into serpentine minerals, including Ni. However, the fine particles were highly enriched rather than deficient with contaminants; therefore, their removal efficiencies were extremely low due to the high surface areas for retaining strongly inorganic contaminants and recalcitrant minerals (Table 2). Further, the concentrations of As in the
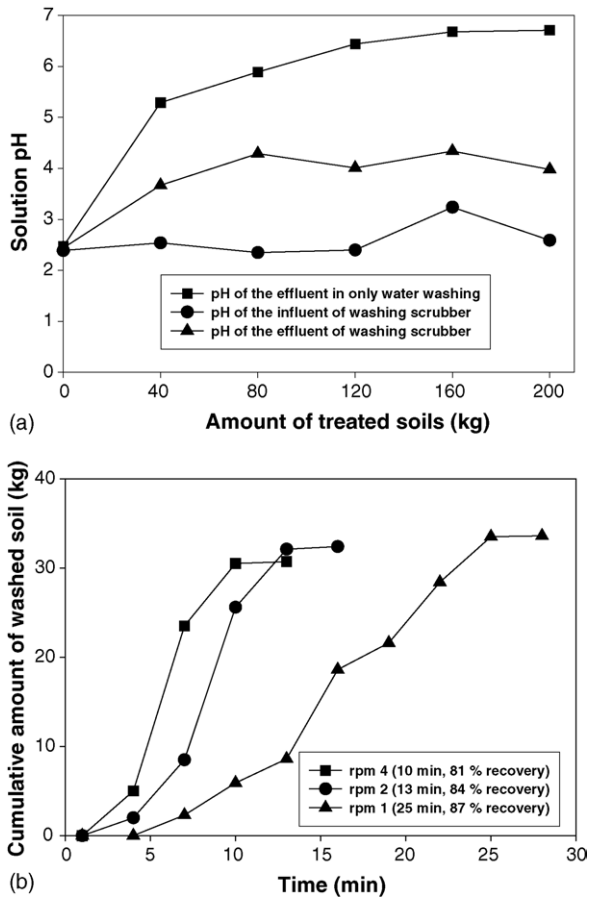
(a)



(b)

Fig. 6. Variation of (a) pH in influent and effluent and (b) recovery of treated soils against reaction time.

production of fine particles of 5–6% (<0.074 mm) or 17–19% (<0.149 mm) was suitable for the overall soil washing process. More than 20% (<0.25 mm) production of fine particles was expected to be less cost-effective [30]. It is also apparent that the acid-attackable fractions such as the exchangeable, Fe/Mn oxide and organic/sulfides fractions can be more favorably extractable than the residual fraction and coarse particles rather than fine particles. Despite the low removal efficiency through chemical extraction of the leachable and bioavailable fractions of contaminants, the physical separa-

fine particles of treated soil were much more enriched than Zn and Ni and even in the exchangeable fraction. Arsenic was enriched in the fine particles, whereas Zn and Ni were enriched in the residual fraction of various particle size fractions rather than fine particles only. The efficiency of the chemical extraction of As was dependent on the fine particles, whereas the efficiencies of Zn and Ni were determined by the residual fraction of various particle size fractions. Although acid solutions were restricted to extract As in the fine particles, $H_3PO_4$ extracted more As than HCl. The washing solution was pH 2–3 in the front compartment and pH 3–4 in the end compartment of the washing scrubber (Fig. 6a). In a less acidic condition of more than pH 2, the solubility of As generally decreases, but Zn and Ni are highly mobile. Arsenic was expected to be more absorbable due to the stronger binding to soil surfaces except those less than pH 1 or in alkaline condition [8].

Table 2 shows the effect of the physical size separation on the removal efficiency with respect to As, Zn and Ni. Because the fine particles were enriched with contaminants, the removal efficiencies were enhanced with a definite volume reduction of fine particles. Considering the removal efficiencies of the chemical extraction of contaminants and the cost-effectiveness for the treatment of fine particles, the
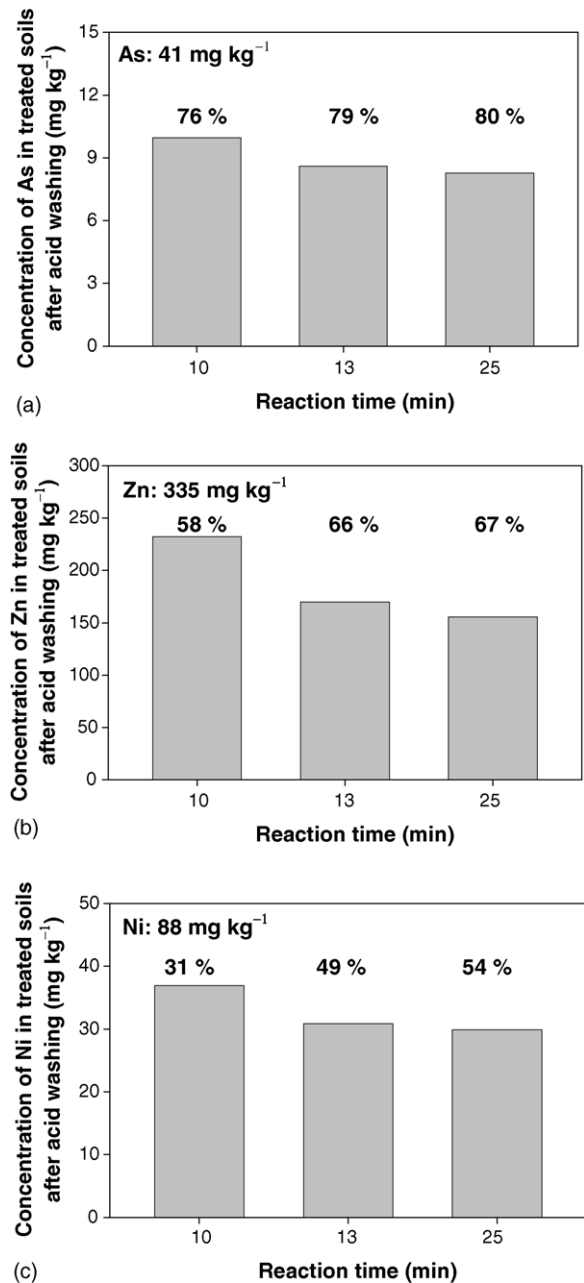


(a)



(b)



(c)

Fig. 7. Removal efficiencies of (a) As, (b) Zn, and (c) Ni with respect to the reaction time of treated soil in the washing scrubber (initial bulk concentrations and removal efficiencies of As, Zn and Ni are given in mg kg$^{-1}$ on the top of each column).

tion of fine particles was ascribed to the overall enhanced effectiveness of acid washing.

### 3.5. Effect of reaction time on acid washing

As reaction time increased from 10 to 25 min, the removal efficiencies of contaminants were also enhanced for HCl-washing (Fig. 7). The removal efficiencies of both $H_2SO_4$- and $H_3PO_4$-washing were also similar to that of HCl-washing (data not shown). Above more than 13 min, the removal efficiencies of contaminants became significantly less. Therefore, the further chemical extraction seemed to be restricted after 13 min. Each fraction of As, Zn and Ni was also extracted gradually (Fig. 8). The concentrations of exchangeable and residual fractions were less variable for reaction times of 13 and 25 min, but the Fe/Mn oxide and organic/sulfides fractions gradually decreased. It is apparent that exchangeable and residual fractions were washed quickly because the detachment of contaminants from easily bound and recalcitrant fractions was instantly determined by the acid attack. In the case of Fe/Mn oxide and organic/sulfides fractions, there was possibly a gradual extraction of As and Zn by an increase in the reaction time.

### 3.6. Monitoring of washing solution and treated soil

The acid washing process in this washing equipment recycles the washing solution only through the precipitation of fine particles in the ceramic filter and removes few dissolved contaminants. Hydrochloric acid used as an acid solution extracted both major elements and As, Zn and Ni during an 11-batch treatment of a total soil weight of 440 kg (Fig. 9a and b). In the recycled washing solution, Ca comes dominantly from calcite mineral in contaminated soil; an instant neutralization reaction between the calcite and the acid solution seems to saturate high concentrations of Ca and partial Mg in the washing solution. This happens because calcite mineral consists of the calcite and dolomite composition including Ca–Mg solid solution. In particular, Al and Fe were the most dominant inorganic elements with an increase of high concentrations. The contaminants such as As, Zn and Ni also increase just in their low concentrations, but the simultaneous increase implies a favorable chemical extraction in the washing scrubber. Despite the slight increase in the washing solution pH (pH 3–4) in the end compartment of the washing scrubber, As seems to be dissolved. However, in the intermediate pH ranges As species can be, to a significant amount,
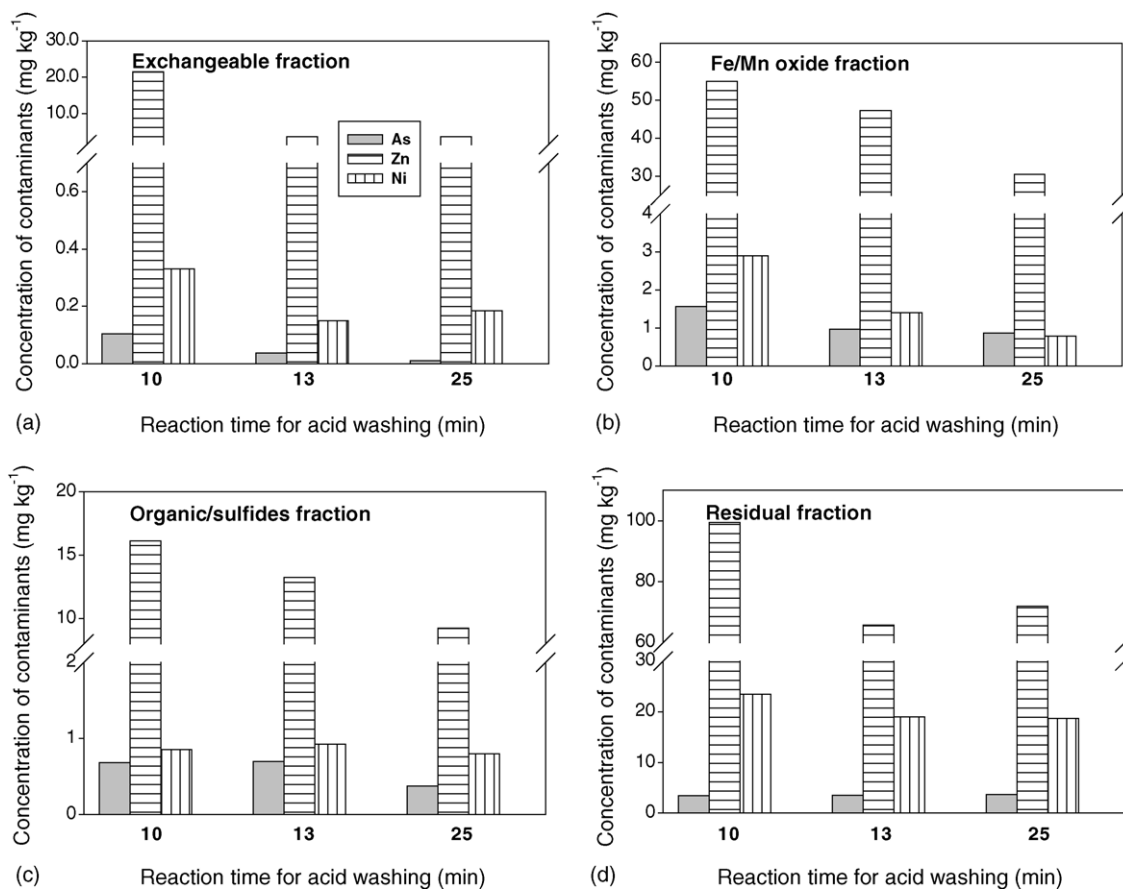


Fig. 8. Chemical fraction of As, Zn and Ni with respect to the reaction time of contaminated soils for HCl washing in washing scrubber: (a) exchangeable fraction, (b) Fe/Mn oxide fraction, (c) organic/sulfides fraction and (d) residual fraction analyzed by BCR sequential extraction method.
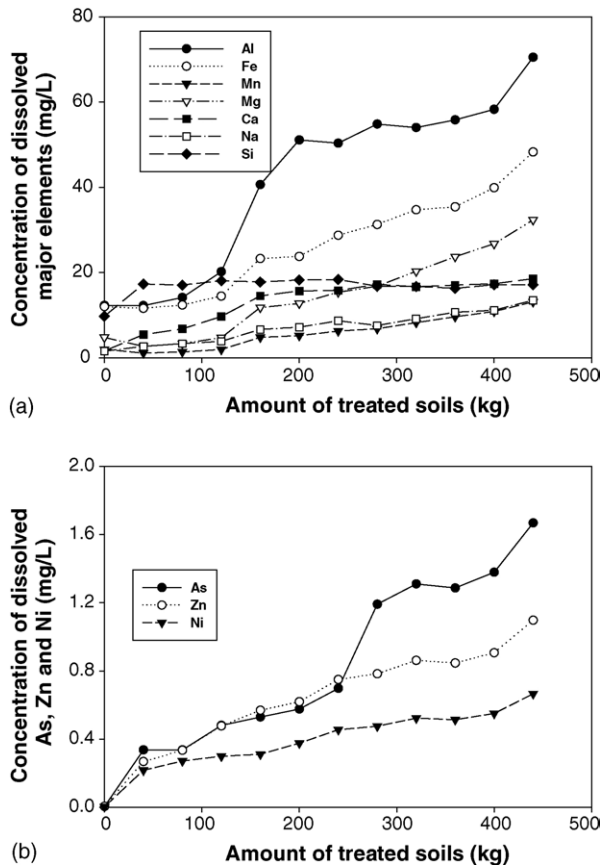
Fig. 9. Concentration of (a) dissolved major elements and (b) contaminants during the acid washing.

able organic matter. The organic matter in the fine particle fraction decreased from 2.8 to 1.1%; the organic matter in the coarse fraction also decreased from 0.5 to 0.2%. It is known that soil organic matter consists principally of litter (macroorganic material lying on the soil surface), the light fraction (plant residues within the soil proper), soil biomass (predominantly microorganisms living in the soil) and stable humus [34]. An acid solution or water may remove the soluble phase and particulate of organic matter, and, specifically, the acid soluble phases of humus seem to be organic fractions, except for humic acid due to its precipitation as acid resistance. Due to the limitation of bioavailable organic matter of acid-washed soil, acid washing is likely to have a detrimental effect on soil property; thus the treated soil can be applied with a restriction such as a non-agricultural and less bioavailable use. The fine particles have more organic matter than the coarse particles due to a high area of reactive surfaces, and play an part in the retention of organic matter.

## 4. Summary and conclusions

The pilot-scale acid-washing of soil contaminated with As, Zn and Ni was assessed with the following conclusions:

1. The simultaneous acid-extraction of both oxyanionic As and cationic Zn and Ni was inhibited to their dominant presence of the residual fraction such as Ni incorporated into serpentine and high acid buffering by the carbonate content. The strong acid solution including the competitive oxyanions was favorable for the simultaneous acid-washing of oxyanionic As and cationic Zn and Ni. Particularly, the competitive oxyanions such as phosphate and sulfate from $H_2SO_4$ and $H_3PO_4$ enhanced As extraction. However, the acid washing of Ni was less efficient due to its recalcitrant mineral incorporation.

2. Acid washing of coarse particles effectively extracted As, Zn and Ni with a significant decrease in their concentrations. Nickel from the residual fraction in coarse particles were less extracted than As and Zn. However, Fe/Mn oxide, organic/sulfides and residual fractions in fine particles less than 0.074 mm were enriched with contaminants because fine particles had high surface areas for retain-

adsorbed onto reactive surfaces such as fine particles or ferric complexes [2,8]. Careful control of the pH to keep it to a low pH (less than 2–3) is needed during the recycle process of the washing solution.

During acid washing, the acid solution significantly affected the chemical properties of the soil. The treated bulk soil after acid washing became acidic, and, particularly, the soil pH (pH 3.3) of the fine particles was more acidic than that (pH 5.7) of the coarse particles (Table 3). The acid buffer capacity in fine particles was large enough to keep a low pH for the treated soil. Correspondingly, a suitable post treatment like neutralization can be needed, particularly in fine particles. Acid washing also led to the removal of consider-

Table 3
Change of chemical properties in treated soil during the soil washing experiment

| Analysis | Unit | Value | | Measurement |
|---|---|---|---|---|
| | | Before acid washing | After acid washing | |
| Water content | % | 4.6 | 15.6 (13.1–25) | Drying at 100 °C |
| Organic matter | % | 1.2 (bulk soil) | – | Ignition at 450 °C |
| | | 0.5 (>74 μm) | 0.2 (0.1–0.4) (>74 μm) | |
| | | 2.8 (<74 μm) | 1.1 (1.0–1.3) (<74 μm) | |
| Soil pH | – | 7.7 (bulk soil) | – | pH in water |
| | | 7.6 (>74 μm) | 5.7 (5.4–6.3) (>74 μm) | |
| | | 7.9 (<74 μm) | 3.3 (3.1–3.5) (<74 μm) | |

ing strongly inorganic contaminants and further partially consisted of recalcitrant minerals. Arsenic was enriched even in the exchangeable fraction of fine particles less than 0.074 mm. It was expected that As was more absorbable except for in the presence of competitive oxyanions for $H_2SO_4$ and $H_3PO_4$ washing due to the stronger binding to soil surfaces in a less acidic condition (>pH 2). In addition, Zn and Ni were enriched in residual fraction of various particle size fractions rather than fine particles only. Therefore, the efficiency of chemical extraction of As was dependent on the fine particles, whereas those of Zn and Ni were determined by the residual fraction of various particle size fractions.

3. The physical size separation removed the finer particles including high contents of contaminants. The production of fine soil particles of 2.4% (<0.074 mm) and 7.5% (<0.149 mm) was suitable for the overall effectiveness of the soil washing. Despite the low removal efficiency through the chemical extraction of the acid-attackable fraction such as the exchangeable, Fe/Mn oxide and organic/sulfides fractions, the physical separation of fine particles was ascribed to the enhanced effectiveness of acid washing. Therefore, the overall efficiency of soil washing increased by both the acid-extraction and physical size separation.

4. The exchangeable and residual fractions were less variable above more than 13 min with the limit of the further chemical extraction because the detachment of contaminants from easily bound and recalcitrant fractions were instantly determined by the acid attack. In the case of Fe/Mn oxide and organic/sulfides fractions, there are possibly a gradual extraction of As and Zn by an increase of reaction time.

5. The treated soil after acid washing lost organic matter and became acidic. Particularly, acid washing could give the detrimental effect on soil due to the limitation of bioavailable organic matter. The acid solution extracted major elements with a concomitant increase of high concentrations and those of As, Zn and Ni also increase just in their low concentrations, implying a favorable chemical extraction of both oxyanionic and cationic contaminants in the washing scrubber. However, the slight increase of the washing solution pH occurs in the end compartment of the washing scrubber. Careful control of the pH to keep it to a low pH (less than 2–3) is needed during the recycle process of the washing solution for the removal of As during the removal of cationic metals.

## Acknowledgements

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