



Extraction behavior of As, Pb, and Zn from mine tailings with acid and base solutions

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ABSTRACT

The aim of this study was to investigate the extraction behavior of As, Pb, and Zn from mine tailings for considering the feasibility of soil washing. Extraction of metals was studied for different extractant doses, solid/liquid ratios, and equilibrium times. Generally, high extraction efficiency was achieved with HCl, H₃PO₄, and H₂SO₄, while H₂SO₄ proved to be problematic with respect to Pb. NaOH was found to be favorable in removing As, while it was not effective at extracting Pb and Zn. With optimum conditions, which were a 1:5 solid–liquid ratio and 2 h of extraction time, 0.5 M of HCl extracted 21.1–72.5%, 9.9–86.5%, and 6.1–74.1% of As, Pb, and Zn, respectively. The power and Elovich function were adequate to describe adsorption kinetics. These results suggest that HCl and NaOH could be used to effectively extract all metals without selectivity and As with selectivity, respectively, in mine tailings and could be used for the design of soil washing process.

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1. Introduction

There are many abandoned mines contaminated with metals in Korea [1]. According to the Ministry of Knowledge Economy, approximately 2000 abandoned mines exist in Korea. Metals leached from abandoned mines have caused serious problems in relation to human health and ecological implications. Mine tailings have high concentrations of As, Pb, Hg, Cr, Zn, Ni, Cu, and Cd, which are highly toxic and carcinogenic. Because these are not degradable and exist persistently in the environment, proper treatments are required.

Generally, the remediation methods for metal-contaminated soil in mining sites have been excavation/disposal and solidification/stabilization [2]. These methods are not a permanent treatment method because (a) continuous monitoring is needed, (b) the metals are not removed from the soil, and (c) the long-term stability of the solidification/stabilization is questionable [3]. The alternative technologies (in opposition to conventional options based on ex situ stabilization/solidification and off-site disposal) mostly selected for treating metal-contaminated soils and mine tailings include: (1) metal extraction techniques such as soil washing, phytoextraction, and electrokinetic remediation; (2) in-situ metal immobilization techniques such as phytostabilization and in situ bio-chemical fixation/stabilization (soil amendments with

inorganic and organic compounds) [4–7]. Among these alternative technologies, a wide array of physical, chemical or biological techniques of soil washing processes have been evaluated and successfully used in numerous field-scale remediation projects for permanently removing the metals from contaminated soils [3–7]. In recent years, attention has focused on the development of in situ alternative methods (such as phytoremediation, in situ chemical stabilization, bioremediation and soil flushing) that are generally less expensive and disruptive than conventional excavation, treatment and disposal methods [8]. However, the soil washing via chemical extraction methods presents several advantages compared to in situ immobilization and phytoremediation techniques: (1) the rapid revitalization of the site since the contaminated materials are excavated; (2) the short duration of the soil washing process; (3) the volume reduction of contaminated soil; (4) the possibility of metal recovery by extracting the dissolved metals from the washing effluents [3,4]. The migration of metals from soil to aqueous solutions occur by (a) changes in the pH, (b) changes in the ionic strength, (c) changes in the redox potential, and (d) the formation of complexes, and (e) the ligands/ions exchange reactions [3,9]. Generally, solutions containing inorganic acids, organic acids, chelating agents, inorganic salts, bases, or surfactants can be used in soil washing [1,7,9–12]. However, the simultaneous treatment of cationic metals (Cu, Cd, Ni, Pb, Zn, etc.) and anionic arsenic contaminants may be difficult or ineffective with the same extracting reagents due to their dissimilar chemical properties. Particularly, the chemical leaching methods recently investigated for the removal of arsenic from the contaminated soils involves var-

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ious extractants: (1) acid reagents; (2) alkaline reagents; (3) salt reagents containing phosphates; (4) biological processes. The main mechanisms involved in the release of arsenic from soils to washing solution includes desorption and dissolution processes. The most important chemical factors to control the arsenic extraction are the pH and redox reactions [11,13,14].

In this study, the extraction behavior of metals in mine tailing was investigated. Various acid and base extractants were used to extract metals from mine tailings. By optimizing the operating parameters, the concentration of the extractants, solid/liquid ratio, and extraction time were changed. Especially, this study was made of the feasibility of soil washing to remediate contaminated mine tailings with a high arsenic concentration and relatively low lead and zinc concentrations.

2. Materials and methods

2.1. Site description and sampling of mine tailings

The study area, the Songcheon (SC) Au–Ag mine, is located in Yeongok-myeon, Gangneung, Gangwon-do, South Korea. The deposits of SC mine are classified as hydrothermal Au–Ag bearing quartz veins, and the main geology is composed of Precambrian felsic gneiss. The sulfide minerals in this mine consist of arsenopyrite, pyrite, galena, and sphalerite [15]. The SC mine was closed in 1995 and a large quantity of mine tailings and waste was abandoned without proper treatment. Although 8000 m³ of mine tailings were processed by the Mine Reclamation Project in 2006, there are still mine tailings left.

The soil used was sampled from the topsoil layer (0–30 cm) of the SC mine. The soil samples were air-dried and sieved through a sieve with 2 mm holes (10 mesh).

2.2. Extraction of metals

To measure the metal extraction efficiency, batch experiments were conducted using solid–liquid ratios of 1:1–1:10, 0.1–2.0 M of extractant, and 0–360 min of extraction time. As extraction agents, reagent grade HCl (Daejung, Korea), H₂SO₄ (Fluka, USA), H₃PO₄ (Sowha, Japan), and NaOH (Junsei Chemical Co., Japan) were used without further purification. All of the other reagents were obtained from Sigma–Aldrich (USA). Generally, 5 g of soil was inserted into 25 ml of extracting solution in a 50 ml conical tube. The solution was shaken for 60 min at 20 °C and 150 rpm in a shaking incubator. After that, a high-speed centrifuge was used to centrifuge the tube at 3000 rpm for 10 min to separate the extractants from suspension. The metal concentration of the final extractant was analyzed using an induced coupled plasma optical emission spectrophotometer (ICP-OES, Varian 730-ES, USA). In a kinetic study, solutions of 0.5 M of HCl or NaOH containing 5 g of soil were shaken for 5, 10, 20, 30, 60, 120, 180, 240, 300, and 360 min.

Considering the regulation levels of metals in soils by the Republic of Korea, the Korea Standard Test (KST) methods were used. Briefly, (1) add 50 ml of 0.1 M or 1 M HCl to each 10 g of soils for Pb or As, respectively, (2) shake the suspension at 30 °C for 60 min or 30 min for Pb or As, respectively, (3) filter the supernatant using 5B filter (Advantec, Japan), and (5) acidify the filtrate and analyzed the Pb and As concentrations by ICP-OES.

To evaluate the pseudo-total extraction efficiency of metals and Zn content in soils by KST methods with some modification, aqua regia extraction was performed. Briefly, 2.4 ml of aqua regia (HNO₃:HCl = 1:3) was inserted into a test tube containing 0.3 g of soil. The solution was kept in a hood for 16 h to oxidize the organic matter and heated at 70 °C for 2 h in a heating block. Deionized water was injected to make 10 ml, followed by cooling. After vortex

mixing and filtering, the metal concentration in the extractant was analyzed by ICP-OES. Aqua regia extraction provides the pseudo-total metal concentrations, which is not the total concentrations, and the aqua regia extracts 70–90% of the total arsenic in soils of mine sites [1]. All of the batch experiments were carried out in duplicate.

2.3. BCR sequential extraction

To determine metal fractionation in the soil, the BCR three-step sequential extraction procedure was used. The sequential chemical extraction procedures can help in assessing the potential mobility and solubility of metals in contaminated soils. A group in a European Community Bureau of Reference (BCR) project proposed a three-step extraction procedure for the analysis of sediment, soil, sludge, and mine waste [7,16]. The BCR method was developed by Quevauiller et al. [16] and modified by Rauret et al. [17]. The current state of the BCR sequential extraction scheme was summarized by Bacon and Davidson [18]. In the revised BCR sequential extraction, metals presented in soluble forms, which include free ions, soluble complexes, bounded onto a carbonated form, and the exchangeable fractions, were released in step 1. Metals bounded onto Fe and Mn oxides were extracted in step 2. In step 3, metals bounded onto organic matter and sulfides were separated. Finally, the residual fractions of the metals were extracted by aqua regia extraction, which was an internal check step to compare the total aqua regia extractable amounts of the metals and the summarized extracted amounts of the metals in step 1–3. In the BCR three-step procedure, 1 g of mine tailing was used. A brief scheme of the procedure is summarized in Table 1.

2.4. Analysis

To determine the soil pH by KST method, 5 g of air-dried soil was added to 25 mL deionized water (solid to water ratio = 1:5) in a 50 ml beaker and equilibrated for 1 h. The pH value was measured by a pH meter (Mettler Toledo 8603 pH meter, USA) equipped with a pH electrode. The amount of organic matter in the soil was determined gravimetrically by ignition at 600 °C in a muffle furnace. The cationic exchange capacity (CEC) was measured by standard method 9081 in USEPA SW-846 [19]. Soil particle size distribution was determined using the ASTM D 422 method [20].

All extractants were filtered through a 0.45 μm filter and acidified with nitric acid before metal analysis. The concentrations of the metals in the extractants were measured by ICP-OES. The extracted metal concentration in the soil was calculated by the difference between the initial and final concentration in the extractant. In this study, the metals included metalloids (As) and heavy metals (Pb and Zn).

2.5. Kinetic modeling

In order to investigate the extraction mechanism of the metals from soils, frequently used kinetic models were used (Table 2) [21–25]. The kinetic models were fitted to the metal extraction data using linear regression analysis with SigmaPlot (ver. 10, Systat Software, Inc.). Their goodness of fit was evaluated based on the coefficient of determination (r^2) and the standard error of estimation (SEE), calculated by:

$$SEE = \left(\frac{\sum (q_t - q'_t)^2}{n - 2} \right)^{1/2}$$

where q_t and q'_t are the measured and estimated mole fraction of extracted metals at time t , respectively, and n is the measured number.

Table 1
BCR sequential extraction scheme [18].

	Reagent	Fraction label	Nominal target phases
Step 1	0.11 mol l ⁻¹ CH ₃ COOH, 16 h shaking (22 ± 5 °C)	Exchangeable, water- and acid-soluble	Soluble and exchangeable cations, and carbonates
Step 2	0.5 mol l ⁻¹ NH ₂ OH.HCl at pH 1.5, 16 h shaking (22 ± 5 °C)	Reducible	Fe–Mn (oxy)hydroxides
Step 3	H ₂ O ₂ (85 ± 2 °C) then 1 mol l ⁻¹ CH ₃ COONH ₄ , 16 h shaking (22 ± 5 °C)	Oxidisable	Organic matter and sulfides
Step 4 ^a	Aqua regia	Residual	Residual

^a This step is not an official step.

Table 2
Linear kinetic equations to describe metal extraction mechanism [41].

Kinetic model	Equation ^a
First-order	$\ln Q_t = \ln Q_0 - k_1 t$
Second-order	$1/Q_t = 1/Q_0 + k_2 t$
Power function	$\ln q_t = \ln(k_p Q_0) + 1/m \ln t$
Elovich	$q_t = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t$
Parabolic equation	$q_t = B + k_d t^{1/2}$

^a Q_t and Q_0 are the mole fraction of metals in soils after the desorption period $t = t$ and $t = 0$, respectively, q_t is the mole fraction of metals desorbed by extractants after desorption period t , and k_1 , k_2 , k_p , k_d , B , α , and β are constants.

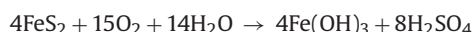
3. Results and discussion

3.1. Characteristics of mine tailings

The physico-chemical properties of the soils are summarized in Table 3. The pH of SC1, SC4, and SC5 ranged from 6.2 to 6.7. The pH of SC2 and SC3 was 4.57 and 2.97, respectively. The organic matter content of SC2 was 4.13% and that of the others was around 1%. The CEC of all the soil samples was below 10 cmol kg⁻¹ except for SC3 which had 26.3 cmol kg⁻¹ of CEC. Based on the particle size analysis, the classifications of SC1, SC2, SC3, and SC4, and SC5 were sandy clay loam, sandy clay, sandy loam, and light clay, respectively.

There are important factors that significantly influence the metal extraction by soil washing process: e.g., the metal distribution according to the grain size of soil, the characteristics of the washing solution (pH, Eh, nature and concentrations of reagent) and the experimental parameters of washing systems (batch or column mode, particle-size distribution, agitation rate, L/S ratio, etc.) [9]. In general, an increase in the soil pH, CEC, or organic matter contents inhibited the metal's extractability and mobility [3]. In the case of SC2, the pH was low and the contents of iron and sulfide were 6.6% and 2.6%, respectively. The results indicate that SC2 may include sulfite ores containing minerals existed as arsenopyrite (FeAsS), pyrite (FeS), galena (PbS), and sphalerite (ZnS) [15]. The acidity of SC2 originated from the weathering of pyrite (FeS) in solutions containing dissolved oxygen, which came from rain [26]. When pyrite reacts with oxygen, acid mine drainage (AMD) is formed by pyrite oxidation, ferrous iron oxidation, ferric iron hydrolysis, and the enhanced oxidation of pyrite [27]. The total reaction of AMD formation is

shown below:



AMD is rich in sulfate and dissolved metals and has an acidic pH due to the oxidation of the sulfide containing minerals. AMD produces iron, which eventually precipitates as iron oxides. In addition, previous studies mentioned that iron oxides have a high adsorption ability for As [28,29]. SC1, SC3, and SC4 had low organic matter contents and a high proportion of sand. In contrast, SC2 showed high values of CEC and clay fraction and SC5 had high silt and clay fraction (90.5%). In soil washing, the proportion of sand needs to be in excess of 50–70% for the effective and economical removal of metals [3]. According to the soil characteristics, the metals in SC2 and SC5 were not easy to extract.

The arsenic concentrations of this study area were higher than 6 mg kg⁻¹, which is the concerning level of the Soil Environment Conservation Act of Korea (K-SECA) legislated by Korean Ministry of Environment (K-MOE) [30]. The As concentrations (mg g⁻¹) of SC1, SC2, SC3, SC4, and SC5, determined by KST method, were 1.587, 26.990, 3.574, 0.750, and 1.638, respectively. The lead concentrations of tested soils except SC5 were lower than the concerning level of K-SECA (100 mg kg⁻¹). The Pb concentrations (mg kg⁻¹) in SC1, SC2, SC3, SC4, and SC5 were 21, 38, 16, 15, and 114 mg kg⁻¹, respectively. The zinc concentration (mg kg⁻¹) was 429, 187, 91, 459, and 939 mg kg⁻¹ for SC1, SC2, SC3, SC4, and SC5, respectively. The zinc concentrations of SC1, SC2, SC4, and SC5 were higher than the concerning level of K-SECA, which is 300 mg kg⁻¹.

As seen from the aqua regia extraction, the concentration of As in the mine tailings was extremely high (Table 4). The aqua regia extractable concentrations of As, Pb, and Zn were 1941–37, 145, 61–9,941, and 92–939 mg kg⁻¹, respectively. The amount of iron in the soil samples was 14,312–63,686 mg kg⁻¹. The amounts of Ca and Mg in SC1, SC4, and SC5 were 2887–4997 and 4062–5659 mg kg⁻¹, respectively, whereas in SC2 and SC3 they were 162–382 and 334–690 mg kg⁻¹, respectively.

The metal fractionation in the soils determined by BCR sequential extraction was residual and Fe–Mn oxide bounded fractions (Fig. 1). In the case of SC1 and SC3, As and Pb mainly existed as residual fractions and Fe–Mn oxide bounded fractions. The residual fraction of Zn was 73% and 63% for SC1 and SC3, respectively. In the case of SC2, the residual fractions of As, Pb, and Zn were 80.9%, 93.9%, and 90.1%, respectively. Lead was presented mainly in an Fe–Mn oxide bounded form in SC4 and SC5 and Zn existed as extractable and carbonated forms in SC5. In the acid extraction for mine tailings, the extractable and carbonate fractions of metals were extracted first and then the Fe–Mn oxide bounded and organic matter/sulfide bounded fractions were dissolved by acid [7]. Conclusively, the Zn and Pb in SC4 and SC5 might be easily extracted by acid, according to the fractionation of the metals in the soil determined by the BCR sequential extraction. However, the result of sequential extraction should be carefully interpreted. A mass transfer and redistribution of metal may occur between com-

Table 3
Selected properties of the soils used in this study.

	SC1	SC2	SC3	SC4	SC5
pH	6.68	2.97	4.57	6.49	6.28
Organic contents (%)	0.34	4.13	0.55	0.24	1.07
CEC (cmol kg ⁻¹)	4.9	26.28	8.22	3.93	9.41
Particle size (%)					
Sand	81.0	61.3	84.0	82.7	9.5
Silt	2.6	12.9	2.8	3.7	53.9
Clay	16.4	25.8	13.2	13.6	36.6

Table 4
Aqua regia extractable metal concentrations (mg kg⁻¹).

Soil	Al	As	Ca	Cd	Cu	Fe	Mg	Mn	Ni	Pb	Zn
SC1	1,296	2,772	2,887	2	26	20,684	4,062	233	14	61	430
SC2	3,080	37,145	162	3	158	63,686	334	38	5	9,942	187
SC3	2,239	4,366	382	1	10	14,312	690	57	5	148	92
SC4	1,457	1,941	4,997	2	37	21,410	5,375	266	19	155	459
SC5	4,158	6,978	4,057	4	73	36,117	5,659	330	35	348	939

partments during extraction and separation. Inaccuracy can result from operational inconsistency during extraction and solid–liquid phase separation procedures [18]. Especially, the BCR sequential extraction has not commonly been used to study arsenic because it is not considered to supply the information needed, in particular with respect to binding to oxides [14,31,32]. The availability of arsenic from mineral phases is dependent on the mineral solubility and dissolution kinetics under the extraction conditions [13]. So, BCR sequential extraction procedure provides comparative information relating to the relative contribution of the target compound and the metal mobility [7,33]. To know the accurate fractionation of arsenic, mineralogical and spectroscopic analysis are needed to validate the operationally defined sequential extraction results for arsenic [13,14].

3.2. Effect of extractant concentration

When HCl, H₃PO₄, H₂SO₄, and NaOH were used as extractants, the removal of metals increased with the concentration of the extractants up to 0.5 M, with little fluctuation above 0.5 M of extractants (Fig. 2).

In all of the tested soils, the extraction efficiencies for arsenic for the tested extractants were similar when above 0.5 M of extractants were used (Fig. 2: A-1–A-5), except for HCl. As the HCl concentration increased from 0.5 M to 1.0 M, the percentage of arsenic removal also increased to approximately 20%. At concentrations of 0.1 and 0.2 M, the arsenic extraction ability increased in the order of H₂SO₄ > H₃PO₄ > HCl, while the removal efficiency was similar for each of the acid solutions used above 0.5 M.

Speciation and leaching of arsenic in soils are highly dependent on the characteristics of the soil environment and the extract solution (pH, redox potential, and the presence of competing

anions). In general, the removal of arsenic from soils by extractants may involve: oxidation/dissolution of arsenic-bearing sulfides (e.g., arsenopyrite); reductive dissolution of arsenic-bearing Fe oxides; acid dissolution of Fe/Al/Mn oxides containing arsenic; and desorption of arsenic from Fe/Al/Mn oxides by ion/ligand exchange [1,8,11].

For the remediation of As-contaminated soils, the extraction of metals from soils with inorganic acids primarily aims the desorption enhanced by low pH, the dissolution of discrete metal compounds, and the dissolution of specific soil components contained metals (e.g. Fe–Mn oxides) in order to obtain indirect release of arsenic [8,9]. However, when the phosphoric acid and sulfuric acid are used as extracting reagent, two processes are involved: (1) the acid dissolution of soil components, and (2) the ligand exchange mechanism due to the presence of competing oxyanions (phosphate or sulfate) in solution [7,8,11]. Additionally, sulfate and phosphate ions in acid solutions inhibit the re-adsorption of arsenic by competitive adsorption onto same adsorption sites [7,8]. Therefore, the advantages of phosphoric and sulfuric acids are high extraction efficiency of arsenic at low acid concentration and rapid extraction.

Arsenic was also significantly removed by NaOH solution. The arsenic removal efficiency for NaOH was similar or slightly higher than that with acid. Arsenic bounded onto soil was exchanged with hydroxyl ions through ion exchange because OH⁻ anions have a higher affinity than other anionic species and high pH conditions prevent re-adsorption of arsenic [1,11,34]. These results support that sodium hydroxide solution can selectively extract arsenic from soils with high efficiency. Alam and Tokuniga [11] reported that As(III) would be mobilized in acidic reducing conditions and that As(V) would be most leachable in alkaline conditions: (1) the maximum extraction of total arsenic was obtained in alkaline condition

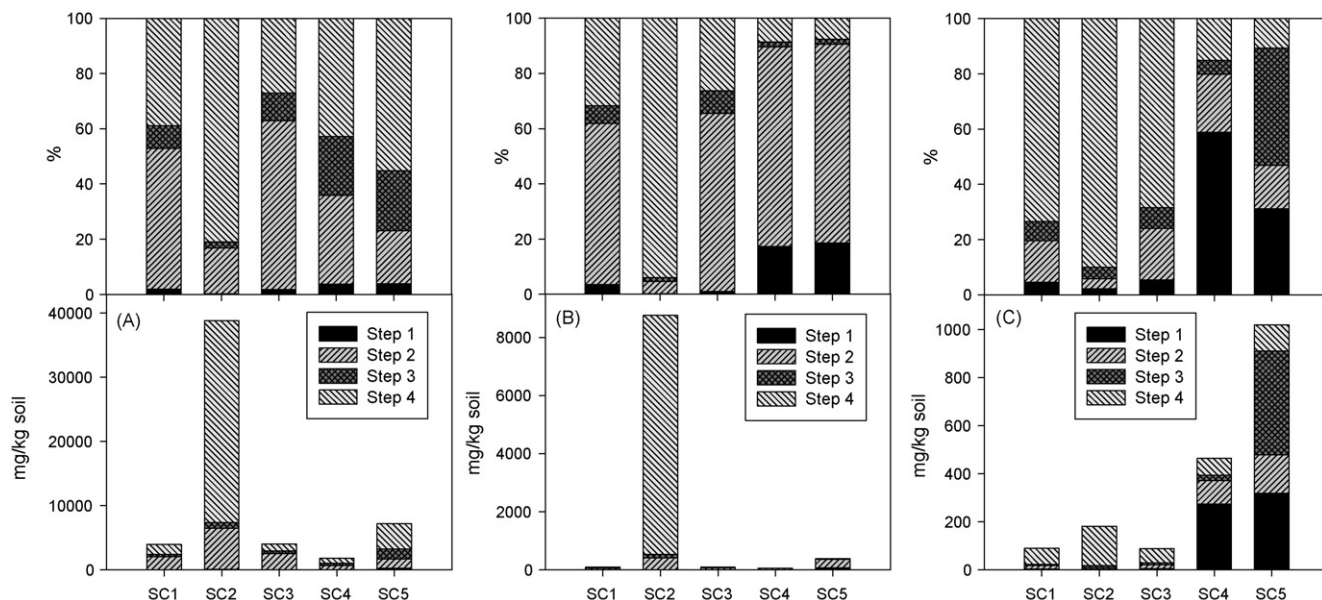


Fig. 1. Distribution of (A) As, (B) Pb, and (C) Zn in mine tailings as determined by BCR sequential extraction.

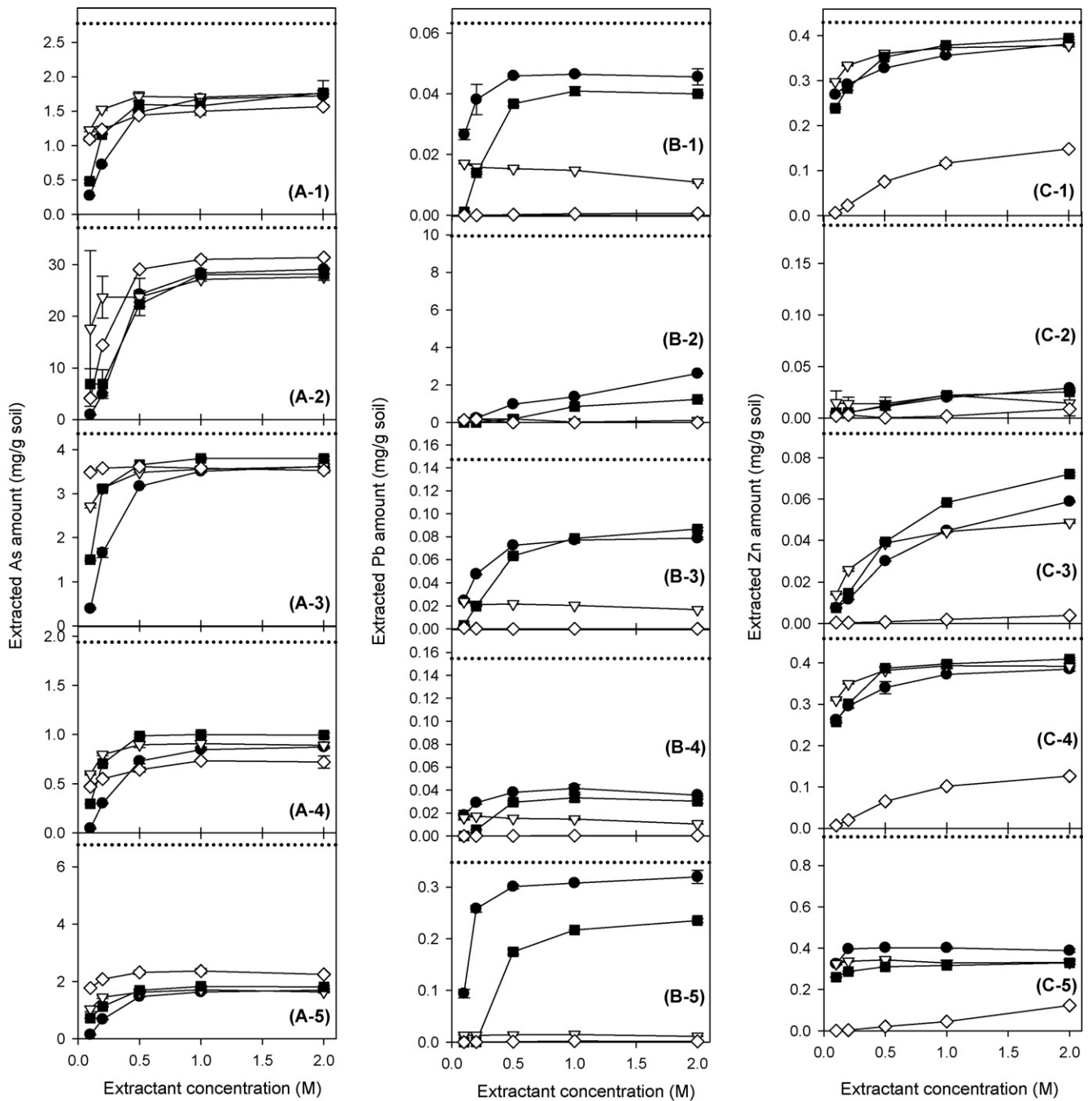


Fig. 2. Extracted amounts of (A) As, (B) Pb, and (C) Zn (mg/g soil) using different concentrations of HCl (●), H₂SO₄(▽), H₃PO₄(■), and NaOH(◇) in soil washing tests (solid:liquid = 1:5). Dashed line (...) indicates the extracted amounts of As, Pb, and Zn (mg/g soil) with aqua regia. Number labels mean the soil number.

(pH > 11); (2) in acidic condition (pH < 2), the maximum extraction of As(III) was obtained but under alkaline condition the extraction efficiency of As(III) was insignificant; (3) the maximum extraction of As(V) was obtained under alkaline condition (pH > 11) but in acidic condition, the extraction efficiency of As(V) was low; (3) in alkaline condition (pH > 11), As(III) was fully oxidized to As(V). Based on these results, NaOH was the most efficient extractant in the removal of arsenic compared to acid extractants. However, NaOH was particularly ineffective in extraction of As(III). Arsenic associated with organic matter in soil could be also leached under alkaline conditions, as humic matter is extracted from soils with strong caustic conditions [25]. In this study, the extracted solution with high concentration of NaOH for SC2, which has 4.13% of organic matter, had high humic matter.

The various extractants showed different patterns for their lead removal efficiency. The lead extraction efficiencies with HCl and H₃PO₄ increased with an increase in extractant concentration and reached a plateau above 0.5 M of extractant. When NaOH was used as an extractant, the soil pH reached a base condition and an insoluble precipitant as a Pb(OH)₂ was made. As this precipitation was at high pH, the lead removal efficiency with NaOH was extremely low. With sulfuric acid, the amount of lead dissolution decreased with an increase in acid concentration. Because the lead forms insoluble PbSO₄ in the presence of SO₄²⁻, an increase in the acid concentration led to the formation of PbSO₄ precipitants. Though PbSO₄ is an insoluble precipitant, some amount of it is dissolved in a strong acid solution. Therefore the lead removal efficiency with H₂SO₄ was higher than with NaOH.

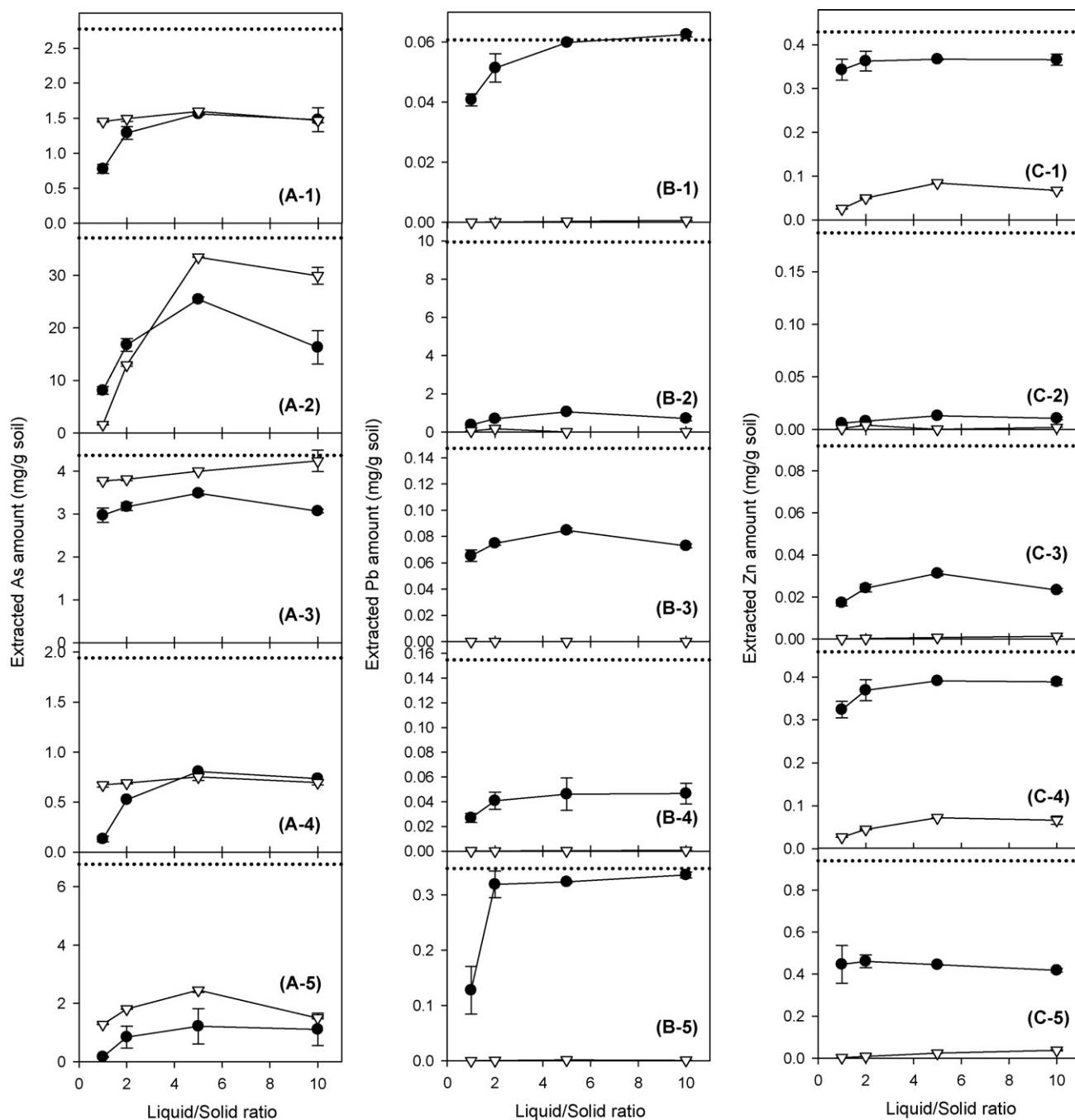


Fig. 3. Extracted amounts of (A) As, (B) Pb, and (C) Zn (mg/g soil) using different liquid/solid ratios with 0.5 M of HCl (●) and NaOH (▽) in soil washing tests. Dashed line (...) indicates the extracted amounts of As, Pb, and Zn (mg/g soil) with aqua regia. Number labels mean the soil number.

The zinc removal efficiency was similar to lead, except for extraction with NaOH. The extracted amount of zinc increased with an increase in the NaOH concentration and was nearly 20–25% of the amount extracted with acid. As the soil pH increased, the speciation of zinc in basic aqueous solutions varied from ZnO to $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$, which are dominant species over pH 11.5 calculated by the MINEQL+ (ver. 4.5, Environmental Research Software).

3.3. Effect of solid/liquid ratio

The optimum solid-to-liquid ratio was 1:5 to remove As, Pb, and Zn in mine tailings with HCl and NaOH (Fig. 3). In arsenic removal, the removal efficiency was the highest with a solid-to-liquid ratio of 1:5. When the ratio was lower or higher than 1:5,

the extraction ability of HCl decreased (Fig. 3: A1–A5). The As, Pb, and Zn removal efficiencies with NaOH were also maximized at a solid–liquid ratio of 1:5. In the case of SC3, the As removal efficiency of NaOH increased with an increase in the solid-to-liquid ratio (Fig. 3: A-3). The Pb removal efficiency of HCl for SC1 and SC5 also increased with an increase in the solid-to-liquid ratio but the amount of increase was small for S:L > 0.5 (Fig. 3: B-1, B-5). Consequently, a solid-to-liquid ratio of 1:5 was the optimum value for soil washing.

3.4. Extraction kinetics

The time-dependent extraction of metal from soil was fitted with first-order, second-order equations, power function, Elovich,

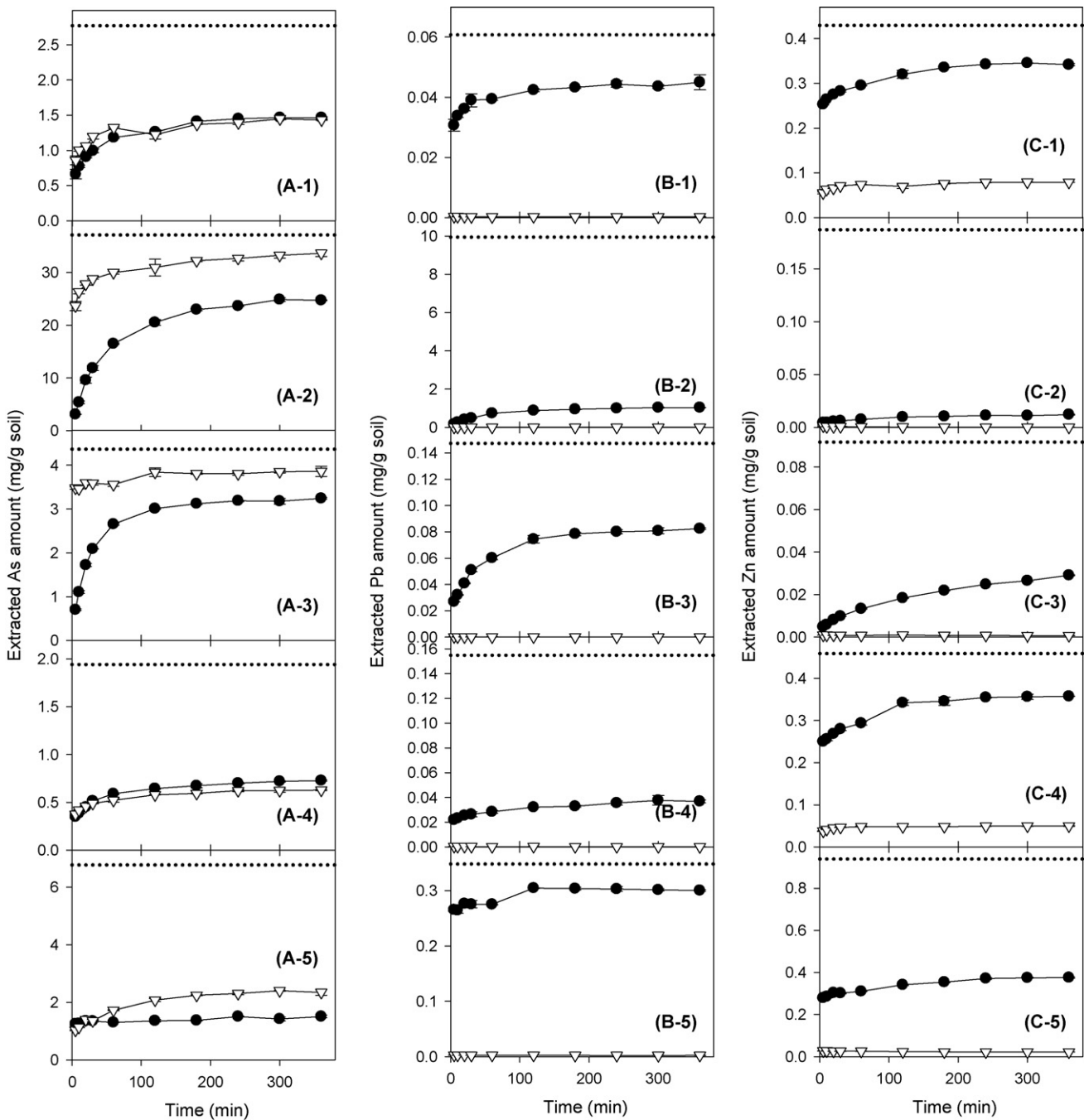


Fig. 4. Extracted amounts of (A) As, (B) Pb, and (C) Zn (mg/g soil) with time using 0.5 M of HCl (●) and NaOH (▽) in soil washing tests (solid:liquid = 1:5). Dashed line (...) indicates the extracted amounts of As, Pb, and Zn (mg/g soil) with aqua regia. Number labels mean the soil number.

parabolic equations (Table 2) and the goodness of fit was evaluated by the coefficients of determination (r^2) and standard error of estimation (SSE). The extraction of As by NaOH was faster than that by HCl and the time to equilibrium in extraction efficiency was about 60 min (Fig. 4). The extraction by 0.5 M HCl reached the equilibrium after 120 min. The acid extraction kinetics of arsenic from soils can be described well with r^2 values of 0.670–0.979, 0.678–0.992, and 0.726–0.917 for the power, Elovich, and parabolic functions, respectively. The HCl extraction of lead can be described satisfactorily with r^2 values of 0.840–0.968, 0.842–0.986, and 0.795–0.938 for those models, respectively, and that of zinc of 0.95–20.998, 0.941–0.973, and 0.931–0.998 for those models, respectively. However, based on r^2 , the arsenic and lead extractions for SC1, SC2, SC3 and SC4 were best described by the Elovich model and that of SC5 by the

power model. Further, the zinc extractions from all of the tested soils were best described by the power model. The NaOH extraction of arsenic can be described satisfactorily with r^2 values of 0.828–0.979, 0.824–0.990, and 0.817–0.938 for the power, Elovich, and parabolic kinetic equations, respectively, where the extraction of lead and zinc with NaOH was not fitted well with those models (mean values of $r^2 < 0.733$). The goodness of fit by SSE was also similar to that by r^2 , but the order of best fitted model based on SSE was slightly different from that based on r^2 . It appeared that the power and Elovich function well described all of the extraction data.

The parameters of extraction kinetic models were summarized in Table 5. Because the second-order equation in adsorption process was reflected a rate-limiting step [35], the equation in the extraction of metals could have a similar meaning. In the Fig. 4, there

Table 5
Parameters of the kinetic models in the extraction of metals by 0.5 M of NaOH and HCl.

Extractant	Metals	Soils	First-order		Second-order		Power		Elovich		Parabolic	
			Q_0	k_1	Q_0	k_2	$k_p Q_0$	m	α	β	B	k_d
0.5 M HCl	As	SC1	0.6802	0.0013	0.6797	0.0023	0.1826	5.2398	0.3624	13.78	0.2475	0.0171
		SC2	0.7592	0.0028	0.7672	0.0056	0.0535	2.1556	0.0458	6.77	0.0938	0.0348
		SC3	0.6067	0.0031	0.5926	0.0077	0.1264	3.0153	0.1120	7.06	0.2359	0.0320
		SC4	0.7689	0.0007	0.7685	0.0010	0.1375	5.6310	0.3526	20.71	0.1833	0.0114
		SC5	0.8151	0.0001	0.8152	0.0001	0.1682	27.1922	7.20.E+07	138.41	0.1781	0.0018
	Pb	SC1	0.4145	0.0015	0.4133	0.0045	0.4572	11.9332	216.0067	19.13	0.5324	0.0120
		SC2	0.9605	0.0002	0.9603	0.0003	0.0106	2.4015	0.0081	45.04	0.0176	0.0052
		SC3	0.7160	0.0017	0.7137	0.0029	0.1234	3.6657	0.1083	10.40	0.1860	0.0226
		SC4	0.8428	0.0003	0.8430	0.0004	0.1108	7.7042	1.0938	41.16	0.1338	0.0060
		SC5	0.2142	0.0018	0.2107	0.0103	0.7064	27.1739	3.80.E+08	33.25	0.7531	0.0072
	Zn	SC1	0.3678	0.0021	0.3705	0.0078	0.5106	12.7927	401.1453	18.37	0.5796	0.0132
		SC2	0.9708	0.0001	0.9708	0.0001	0.0143	3.9030	0.0119	97.07	0.0191	0.0025
		SC3	0.9222	0.0009	0.9252	0.0011	0.0246	2.3033	0.0163	15.74	0.0184	0.0160
		SC4	0.4140	0.0022	0.4156	0.0072	0.4494	10.3952	42.4861	15.75	0.5232	0.0154
		SC5	0.6886	0.0005	0.6890	0.0007	0.2552	13.2671	278.0357	38.23	0.2862	0.0065
0.5 M NaOH	As	SC1	0.6163	0.0008	0.6153	0.0015	0.2763	8.9933	10.5921	21.57	0.3376	0.0107
		SC2	0.2739	0.0033	0.2875	0.0209	0.5881	13.3871	973.4997	17.21	0.6714	0.0136
		SC3	0.1831	0.0017	0.1829	0.0124	0.7570	36.1300	2.16.E+12	42.71	0.7934	0.0057
		SC4	0.7698	0.0004	0.7696	0.0006	0.1625	8.2186	2.8748	31.70	0.1992	0.0075
		SC5	0.8120	0.0007	0.8120	0.0010	0.1032	4.7450	0.1378	19.95	0.1385	0.0121
	Pb	SC1	0.9948	-0.0000	0.9948	-0.0000	5.5956	-13.9082	-4.63E-12	-2.91E+03	0.0056	-0.0001
		SC2	0.9999	-0.0000	0.9999	-0.0000	11.9634	-12.9199	-1.17E-12	-1.28E+05	0.0001	-0.0000
		SC3	0.9989	-0.0000	0.9989	-0.0000	3.4998	-8.4890	-5.45E-08	-4.886	0.0013	-0.0000
		SC4	0.9980	-0.0000	0.9980	-0.0000	-13.6834	-10.7066	-2.06E-11	-6.866	0.0021	-0.0000
		SC5	0.9927	-0.0000	0.9927	-0.0000	11.5080	-22.5734	-7.80E-16	-3.281	0.0076	-0.0001
	Zn	SC1	0.8502	0.0001	0.8501	0.0002	0.1208	13.4968	243.67	85.22	0.1385	0.0027
		SC2	0.9959	-0.0000	0.9959	-0.0000	0.0151	-1.9600	-2.58E-06	-816.92	0.0052	-0.0003
		SC3	0.9900	-0.0000	0.9900	-0.0000	0.0113	-19.0465	-1.51E-14	-2.191	0.0104	-0.0001
		SC4	0.9055	0.0001	0.9054	0.0001	0.0798	17.8783	1.19E+04	185.79	0.0893	0.0012
		SC5	0.9717	-0.0000	0.9717	-0.0000	0.0330	-17.3296	-7.53E-13	-663.32	0.0297	-0.0004

are two distinct regions, which are fast extraction region before 30 min and slow extraction region after 30 min. Although the coefficient of determination was low in the fitting with first-order and second-order equations for whole kinetic data, those equations well matched with each two distinct regions when the data in each region were fitted separately. It means there are rate-limiting steps, and one possible reason is caused by diffusion process, which will be further discussed below. Additionally, the power function was similar to Freundlich isotherm model in adsorption process. The parameter m in the power function is matched with n , which is the heterogeneity factor, of Freundlich isotherm. In the Freundlich isotherm, larger value of n means that there is strong interaction between soil and metals [36]. In this study, larger value (>20) of m indicates the faster extraction of metals. In As and Pb extraction from SC5 with 0.5 M of HCl and As extraction from SC3 with 0.5 M of NaOH, the m values was 27, 27, and 36, respectively, which are higher than 20. At those cases, the extraction was faster than others. In contrast, Saha et al. [23] reported that the parameters of the power function did not define a physico-chemical meaning.

The Elovich model has been frequently used to describe the extraction kinetics of metals [12,22–25,37,38]. The Elovich equation may take care of any irregularities resulting from site heterogeneity and a differing reactivity of sites for the desorption of ions on an irregular surface [23]. According to the assumption of the Elovich equation, one of the two rate constants (α) may be regarded as the rate of an instantaneous rapid reaction and the other rate constant (β) provides the rate of the exponential first-order reaction that took place simultaneously but extended over a period of time [39]. It has been suggested that an increase in α or β^{-1} would increase the reaction rate [39]. The α and β varied widely with soils and extractants. The α and β values for arsenic extraction varied from 0.04 to 2.16×10^{12} and from 6.77 to 138.41, respectively. The soils in which a fast extraction of metal was shown in the initial stage had relatively large α values. These appeared in arsenic and lead extrac-

tions in SC5 with HCl, arsenic extraction in SC3 with NaOH, and zinc extraction in SC4 with NaOH. When Pb and Zn were extracted with NaOH solutions, some of α and β had minus values. It caused by re-adsorption or precipitation with its hydroxide forms.

The parabolic equation describes an intraparticle diffusion [40]. In this model, if extraction of metals is controlled by the intraparticle diffusion process, a plot of q_t versus $t^{0.5}$ gives a straight line. In the kinetic results, the parabolic equation has a high correlation with the results of the extraction with HCl. It means that the extraction of metals with acid solutions was affected by the intraparticle diffusion, which is a rate-limiting step.

4. Conclusion

An evaluation was made of the feasibility of soil washing to extract As, Pb, and Zn from mine tailings using various extractants, and the operating conditions were optimized. Hydrochloric and phosphoric acid extracted all of the metals effectively, sulfuric acid had an effective extraction power for As and Zn, and sodium hydroxide was effective for arsenic. Therefore, to extract metals non-selectively, hydrochloric acid was the best extractant, while sodium hydroxide was a powerful extractant to extract arsenic selectively. With optimum conditions, which were a 1:5 solid-liquid ratio and 2 h of extraction time, 0.5 M of hydrochloric acid extracted 21.1–72.5%, 9.9–86.5%, and 6.1–74.1% of As, Pb, and Zn, respectively. In extraction kinetics, the time dependent extraction data could be best described by Elovich model. In addition, the characteristics of the mine tailings affected the metal extractability. The metal fractionation in the soils was evaluated using the sequential extraction technique, allowing the extractability of the metals to be roughly estimated. However, the relationship between metal extractability and fractionation is not yet clear. Therefore, further detailed researches are needed to understand the mechanism between metal extraction and soil properties.

The soil washing with acidic and alkaline solutions has some limitation. Most of metals exist as residual fraction, which is stable and it is very hard to extract by rain or groundwater. Therefore, most of mine tailing have been treated by stabilization/solidification processes (immobilization treatment). But, it is not permanent method. So, extraction methods are used to reduce the metal concentration below regulation levels or the volume of soils [8]. And the treatment duration is short to medium term and the process attempt to permanently remove metals [3]. However, soil washing process requires large equipment and space, use of expensive and hazardous chemicals, and has difficulty to treat soils containing high clay or organic matter contents. Moreover, the washing effluent should be treated. General treatment methods are precipitation, sedimentation, complexation, electrochemical treatments, ion exchange, membrane technologies, and solvent extraction [3]. In the case of this study, the washing effluents containing NaOH and HCl could be treated by mixing together for neutralization and precipitation. Finally, soil washing with acidic and alkaline solutions might be applied to remediate mine tailing to meet the regulation level at specific sites.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.06.021.

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