Thesis for Degree of Master of Science

Application of soil washing process for the remediation of heavy metal contaminated soil around the Jang Hang smelter

by

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Pukyong National University

August, 2014

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장항제련소 주변 중금속 오염토양 복원을 위한 토양세척법 적용

Advisor: Prof. Minhee Lee

by

Enkhzaya Choijilsuren

A thesis submitted in partial fulfillment of requirements for the
degree of Master of Science

in Department of Earth Environmental Sciences,
The Graduate School,

Pukyong National University

August, 2014

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August 22, 2014

Contents

List of Figures

List of Tables

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Abstract

The Jang Hang smelter is well known as a serious heavy metal contaminated area in Korea. The aim of this study is to demonstrate the feasibility of the soil washing process applying to the soil around the Jang Hang smelter, having high concentrations of heavy metals. The soil was sampled from 7 sites (S1 ~ S7) around the Jang Hang smelter for the washing experiments to investigate the heavy metal removal of the soil washing. Batch experiments were performed at the different ratio of soil to washing solution,

different washing time, various kinds of washing solutions and different pH condition to determine the optimal soil washing condition. Heavy metal concentration of S4 soil was the highest among soil samples, suggesting that S4 soil was contaminated with copper, lead and arsenic. The concentrations of copper, lead and arsenic were determined to 2,666.8 mg/kg, 1,229.9 mg/kg, and 248.6 mg/kg, respectively. In this study, the S4 soil of which size was larger than 297 μm in diameter was chosen for the batch experiments because coarse grained particles (>297 μm) showed high concentration of heavy metals and also covered more than 95 % of total soil particles.

Results of washing experiment using various pH conditions suggested that copper and lead removal efficiencies for pH 1 solution were 14 % and 7 %. From the results of batch experiments, the removal efficiencies of arsenic and copper for the soil washing was 92 % and 93 % respectively, when 0.5 M of NaOH solution was used at 1:3 ratio of soil to solution for 1 hour washing. The removal efficiencies of copper and lead were 51 % and 68 %, respectively, with 0.5 M of HNO_3 solution at 1:5 ratio of soil to solution for 30 minute washing. The removal efficiency of arsenic was 41 % with 0.5 M of HNO_3 solution at 1:3 ratio of soil to solution for 30 minute washing. When the washing condition was 1:3 ratio of soil to 0.5 M of HCl solution, copper and lead removal efficiencies were determined as 46 % and 56 %, respectively. In the case of arsenic, the removal efficiency by using 0.5 M of HCl washing solution was 51 % at 1:5 ratio of soil to solution for 30 minute washing.

Because the removal efficiencies of heavy metals for one time washing did not reach the remediation goal (KPWL: Korea pollution warning limit), six consecutive soil washing were performed to satisfy the remediation goal.The accumulative removal efficiency for 0.5 M of HNO_3 (or HCl) solution every washing time was investigated. The accumulative removal efficiency of copper was 97 % after the 5th washing with HNO_3 solution. The accumulative removal efficiency of lead was higher the remediation goal after the 2nd washing with HNO_3 and HCl solutions 1:1 and 1:3 ratio of soil to solution. The removal efficiency of arsenic was over than 100 % after the 4th washing with HCl solution at 1:5 ratio of soil to solution.

The finally, based on the all results and the properties of the soil, the optimal soil washing condition was suggested to remove heavy metals from soil around of the Jang Hang

smelter. It was 1:3 ratio of soil to 0.1 M of NaOH solution for 1 hour.

Key words: Jang Hang smelter, heavy metal contamination, soil washing process

Chapter 1. Introduction

Industrialization is being progressed with the activities of the smelter and the heavy metal contaminations of soil around the smelter becomes serious risk to human health and ecosystems. The Jang Hang smelter was established in the name of Korea smelting Co., Ltd in 1936 and had been played an important role as the non-ferrous metal smelting for more than 50 years. The operation of the Jang Hang smelter continuously contaminated the surface soil and the atmosphere around the smelter, which were seriously contaminated with arsenic, copper, lead, zinc and cadmium.

Soil washing was considered as one of the remediation processes for these soils because the most of the contaminants were concentrated in the coarse grains or attached on the surfaces of the larger particles (USEPA, 2006). Through the washing process, contaminants such as heavy metals can be separated from the soil particles and transfer into the washing solution (Goller et al., 1993; Absolon et al., 2006; USEPA, 2006). In this study, the optimum soil washing condition was investigated to remediate heavy metal contaminated soils.

Chapter 2. Objective

The objective of this study is to determine the optimal soil washing conditions such as solution type, washing time, ratio of soil to washing solution and concentration of washing solution to remediate the heavy metal contaminated soil around the Jang Hang smelter. Results from batch experiments will support the important information for the design of the soil washing process, applying to soils around the Jang Hang smelter.

Chapter 3. Background

3.1 Outline of research area

3.1.1 Research area

The study area is located in the west side of South Korea. For the study, seven soil samples were collected around the Jang Hang smelter in Korea, which had been smelted lead, zinc and copper from 1936 to 1989 (Fig. 1 and Fig. 2). The Korea ministry of environment had implemented the precise investigation for the heavy metal contaminated site around the smelter from 2009 to 2011.

Fig. 1. Location of the Jang Hang smelter area (□) and 7 soil sampling sites (📍).

(a) (b)

Fig. 2. Soil sampling for the research (a: the chimney stack area in the smelter and b: farmland surface soil around the smelter).

3 .1. 2 Geological characteristics

Geology of the Jang Hang smelter area consists Precambrain gneisses and schists, Cretaceous granite and Quarternary alluvium and aeolian deposits (Kim and Shon, 1963). The Jang Hang smelter was built on a breccia layer that is composed of gneiss, granite, schist and quartzite (Kim et al., 1963) (Fig. 3). Soil profile samples were taken from the area consisting of gneiss which is about 100 m apart from the smelter chimney.

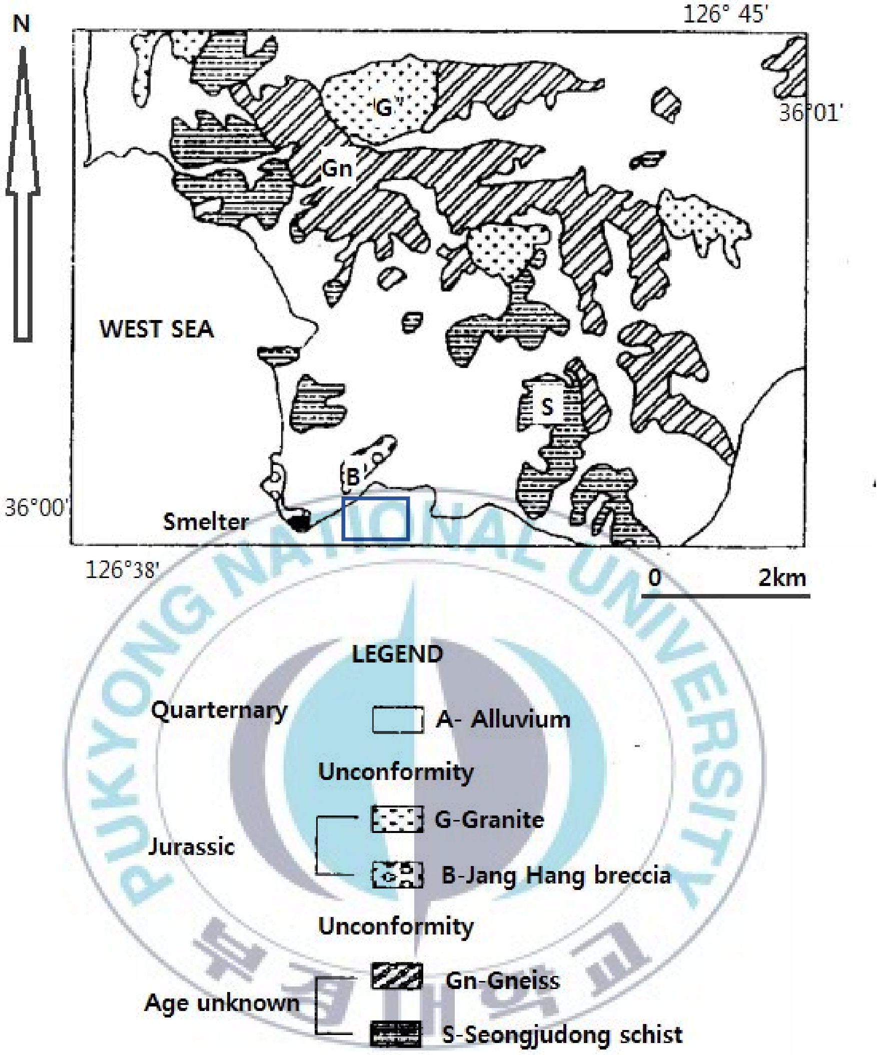


Fig. 3. Geological map around the research area (□) (from Kim et al., 1963).

3.2 Heavy metal contamination in soil

Heavy metals constitute an ill-defined group of inorganic chemical hazards and those most commonly found at contaminated sites are lead (Pb), arsenic (As), cadmium (Cd) and copper (Cu). As the heavy metals enter the human body, terrible diseases such as nerves paralysis, speech impediments and behavior disorder may occur (Kwon and Nam, 2007). Therefore, it is important to decrease the heavy metal pollution and to prevent the leaching of the heavy metal from the contaminated soil. The heavy metals essentially become contaminants in the soil environments such as 1) they become transferred from mines to random environmental locations where higher potentials of direct exposure occur and 2) the chemical species in which a metal is found in the receiving environmental system may render it more bioavailable (Wuana, 2011). Soils are the major sink for heavy metals released into the environment by aforementioned anthropogenic activities and unlike organic contaminants which are oxidized to carbon oxide by microbial action. Most metals does not undergo microbial or chemical degradation (Kirpichtchikova et al., 2006) and their total concentration in soils persists for a long time after their introduction (Adriano, 2003). The presence of toxic metals in soil can severely inhibit the biodegradation of organic contaminants (Maslin and Maier, 2000).

3.2.1 Arsenic

In aerobic environments, As (V) is dominant, usually in the form of arsenate (AsO_4^{3-}) at various protonation states: H_3AsO_4, $H_2AsO_4^{-}$, $HAsO_4^{2-}$ and AsO_4^{3-}. Arsenate and other anionic forms of arsenic behave as chelates and can precipitate when metal cations are present (Bodek et al., 1988). As (V) can also coprecipitate with or adsorb onto iron oxyhydroxides under acidic and moderately reducing conditions. Coprecipitates are immobile under these conditions, but As mobility increases as pH increases (Smith et al., 1995). Under reducing conditions, As (III) dominates, existing as arsenite (AsO_3^{3-}) and its protonated forms (H_3AsO_3, $H_2AsO_3^{-}$ and $HAsO_3^{2-}$). Arsenite can adsorb or coprecipitate with metal sulfides and has a high affinity for other sulfur compounds. Elemental arsenic and arsine (AsH_3), may be present under extreme reducing conditions. Biotransformation (via methylation) of As creates methylated derivatives of arsine, such as dimethyl arsine As $(CH_3)_2$ and trimethylarsine As $(CH_3)_3$, which are highly volatile (Wuana, 2011). Many As compounds adsorb strongly to soils in the netural pH condition and are therefore transported only over short distances in groundwater and surface water. Arsenic is associated with skin damage, increased risk of cancer and problems with circulatory system (Scragg, 2006).

3.2.2 Lead

Typical mean Pb concentration for surface soils worldwide averages 32 mg /kg and ranges from 10 to 67 mg/ kg (Kabata-Pendias et al., 2001). In addition to the inorganic compounds of lead, there are a number of organolead compounds such as tetraethyl lead. The toxicities and environmental effects of organolead compounds are particularly noteworthy because of the former widespread use and distribution of tetraethyl lead as a gasoline additive. Although more than 1,000 organolead compounds have been synthesized, those of commercial and toxicological importance are largely limited to the alkyl lead compounds and their salts. Pb accumulates in the body organs (i.e., brain), which may lead to poisoning or even death. The gastrointestinal tract, kidneys and central nervous system are also affected by the presence of lead (NSC, 2009). Exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Lead performs no known essential function in the human body and it can merely do harm after uptake from food, air or water. The most serious source of exposure to soil lead is through direct ingestion (eating) of contaminated soil or dust.

In general, plants do not absorb or accumulate lead. However, it is possible for some lead to be taken up. Since plants do not take up in plants large quantities of soil lead, the lead levels in soil considered safe for plants will be much higher than soil lead levels where eating of soil is a concern (pica) (Wuana, 2011). Even at soil levels above 300 mg/kg, most of the risk is from lead contaminated soil or dust deposits on the plants rather than from uptake of lead by the plant (Rosen, 2002).

3.2.3 Copper

Copper is the third most used metal in the world (VCI, 2011) Copper is an essential micronutrient required in the growth of both plants and animals. In humans, it helps in the production of blood haemoglobin. In plants, Cu is especially important in seed production, disease resistance and regulation of water. Copper is indeed essential but in high doses it can cause anaemia, liver and kidney damage and stomach and intestinal irritation (Wuana, 2011). Copper normally occurs in drinking water from Cu pipes, as well as from additives designed to control algal growth. While Cu's interaction with the environment is complex, research shows that most Cu introduced into the environment is, or rapidly becomes, stable and results in a form which does not pose a risk to the environment. In the soil, Cu strongly complexes to the organic implying that only a small fraction of copper will be found in solution as ionic copper, Cu(II). The solubility of Cu is drastically increased at pH 5.5 (Martínez and Motto, 2000), which is rather close to the ideal farmland pH of 6.0–6.5 (Eriksson et al., 1997). Cu connection between soil and water contamination and metal uptake by plants are determined by many chemical and physical soil factors as well as the physiological properties of the crops (Wuana, 2011). Soils contaminated with trace metals may pose both direct and indirect threats: direct, through negative effects of metals on crop growth and yield and indirect, by entering the human food chain with a potentially negative impact on human health (Bjuhr, 2007).

3.2.4 Cadmium

Together with Hg and Pb, Cd is one of the big three heavy metal poisons and is not known for any essential biological function. In its compounds, Cd occurs as the divalent Cd(II) ion. In addition, acid rain and the resulting acidification of soils and surface waters have increased the geochemical mobility of Cd, and as a result its surface-water concentrations tend to increase as lake water pH decreases (Campbell, 2006). The application of agricultural inputs such as fertilizers, pesticides, and biosolids (sewage sludge), the disposal of industrial wastes or the deposition of atmospheric contaminants increases the total concentration of Cd in soils, and the bioavailability of this Cd determines whether plant Cd uptake occurs to a significant degree (Weggler et al., 2004). Since the 1970s, there has been sustained interest in possible exposure of humans to Cd through their food chain, for example, through the consumption of certain species of shellfish or vegetables. Cadmium in the body is known to affect several enzymes. It is believed that the renal damage that results in proteinuria is the result of Cd adversely affecting enzymes responsible for reabsorption of proteins in kidney tubules. Cadmium also reduces the activity of delta-aminolevulinic acid synthetase, arylsulfatase, alcohol dehydrogenase, and lipoamide dehydrogenase, whereas it enhances the activity of delta-aminolevulinic acid dehydratase, pyruvate dehydrogenase, and pyruvate decarboxylase (Manaha, 2003). The symptoms are the result of painful osteomalacia (bone disease) combined with kidney malfunction. The major threat to human health is chronic accumulation in the kidneys leading to kidney dysfunction. Food intake and tobacco smoking are the main routes by which Cd enters the body (Manaha, 2003).

3.3 Soil washing process

Conventional process to remediate heavy metals contaminated soils, include soil washing, solidification/ electrokinetic, method and phytoremediation (Lee, 1997). The soil washing process contains advantages, such as short time, low cost and high efficiency for the heavy metals. Soil washing is essentially a volume reduction/waste minimization treatment process. Acid and chelator soil washing are the two most prevalent removal methods (Peters, 1999). Soil washing currently involves, the ex-situ extraction of heavy metals from the soil slurry in reactors and from the soil heap leaching. (Reed, 1995). Removal of the majority of the contaminants from the soil does not mean that the contaminant-depleted bulk is totally contaminant free. Thus, for soil washing to be successful, the level of contamination in the treated bulk soil must be below a site-specific action limit (e.g., based on risk assessment). Cost effectiveness with soil washing is achieved by offsetting processing costs against the ability to significantly reduce the amount of material requiring costly disposal at a hazardous waste landfill (CLAIRE, 2007). Soil washing process is considered as the most widely used techniques in the remediation of soils contaminated with radionuclides and toxic heavy metals (Seeun, 2010). Arsenic, lead and copper content extracted from contaminated soils by soil washing process could be maximized by the use of appropriate pH condition of washing solution and washing time (Mark and Ellen, 2002).

3.3.1 Principles of soil washing

With physical soil washing, differences between particle grain size, settling velocity, specific gravity, surface chemical behaviour and rarely magnetic properties are used to separate those particles which host the majority of the contamination from the bulk which are contaminant-depleted (Dermon et al., 2008). With chemical soil washing, soil particles are cleaned by selectively transferring the contaminants on the soil into solution. Since heavy metals are sparingly soluble and occur predominantly in as sorb state, washing the soils with water alone would be expected to remove too low an amount of cations in the leachates and chemical agents have to be added to the washing water (Davis and Singh, 1995). This is achieved by mixing the soil with aqueous solutions of acids, alkalis, complexants, other solvents and surfactants. The effectiveness of washing is closely related to the ability of the extracting solution to dissolve the metal contaminants in soils. However, the strong bonds between the soil and metals make the cleaning process difficult (Gombert, 1994). Therefore, only extractants capable of dissolving large quantities of metals would be suitable for cleaning purposes. The realization that the goal of soil remediation is to remove the metal and preserve the natural soil properties limits the choice of extractant that can be used in the field (Tejowulan and Hendershot, 1998). The schematic of the soil washing process is shown in Fig. 4.

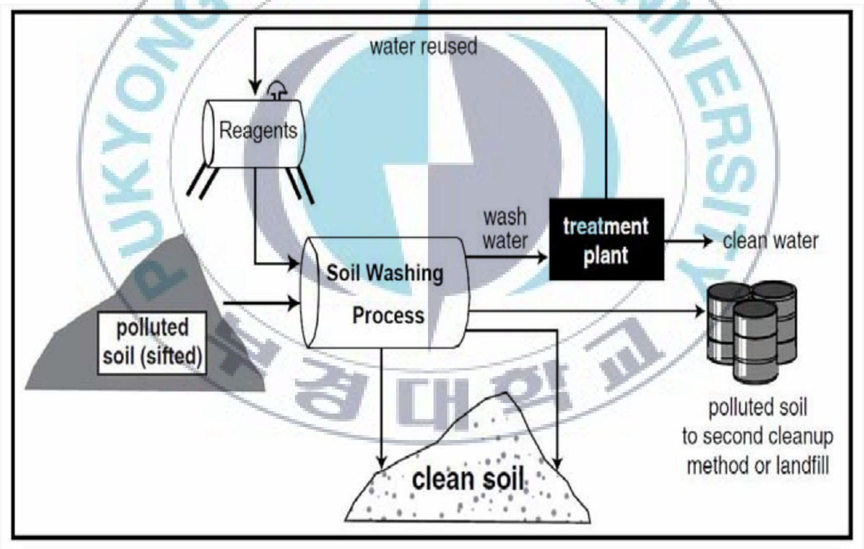


Fig. 4. Soil washing Process Diagram (from Scottish Scientists Export Remediation Tech, 2010).

3.4 Description of soil washing process applied in this study

Batch experiments for the soil washing process to remove arsenic, lead and copper from soils around the Jang Hang smelter were performed in this research. This study was divided into three main experimental sections listed below.

I. Section one contains the investigation for the physicochemical characteristics of contaminated soils. It includes the identification of soil concentration.

II. Section two was composed of batch scale soil washing experiments. The removal efficiencies of arsenic, lead and copper for the soil washing was

III. Section three includes the repetition of washing process to increase the heavy metal removal efficiency until it reaches the remediation limit (KSPWL: Korea soil pollution warning limit) after the soil washing.

CHAPTER.4. Experimental methods

4.1 Materials for the experiment

4.1.1 Soil sampling and analysis for the heavy metal concentration

Arsenic, lead and copper concentration of soil samples collected at 7 sites around the Jang Hang smelter were analyzed according to KSAM (Korean Soil Analysis Method, 2009). Soil samples were dried at 30 °C and sieved with No.100 (0.15 mm in diameter). Three grams of sieved soil samples were mixed with 21 ml of hydrochloric acid and 7 ml of nitric acid in 250 ml round bottom flask, which was left for more than 2 hours on the hot plate (70 - 100 °C) for disintegration. Heavy metals were extracted from soils by using the reflux condenser attached to the neck of the round bottom flask on the hot plate. After extraction, solution in the round bottom flask was filtered with Whatman No. 40 and analyzed on ICP/OES (Perkin-Elmer Optima 7000DV). The analytical process for soil sample is shown in Fig. 5.

(a) Soil sieving (b) Preparation of soil (c) Solvent extraction with strong acids

(d) Filtering (e) Dilution of samples (f) Analysis on ICP/OES

Fig. 5. Process of the aqua regia for the heavy metal concentration analyses.

4.2 Batch experiments

4.2.1 Measurement of soil properties

Several analyses were performed to identify physical and chemical properties of contaminated soil for the experiments. Physical properties such as particle distribution and water content were measured through Korean Soil Pollution standard analytical process (Korea Ministry of Environment, 2009). For the chemical properties, pH of soils was measured by pH meter (Orion 3-star Plus pH Meter) at 1:5 ratio of a soil to distilled water.

4.2.2 Determination of cut off size for the soil washing

It is considered that if the content of fine size particle in the soil is above 25 %, the soil washing will not be effective to remove heavy metal from the contaminated soil. More granular particles are better suited to the soil washing than cohesive or semi cohesive small particles (F.L.I, 2014). S4 soil sample was used to determine the cut-off size for the soil washing because its heavy metal concentrations were very high. The S4 soil particles were divided into seven groups based on their sizes. Afterward, As, Pb and Cu concentrations of each group were analyzed and the result was plotted on the grain size to the concentration diagram. For the grain size analysis, the collected soil sample was dried at 30°C and then 300 g of pulverized soil was sieved by the automatic sieves. The mass of sieve soil particles was represented as the weight percent according to their size ranges to determine the cut-off size for the soil washing.

4.2.3. Batch experiment with various pH of washing solution

Batch experiments of the soil washing were performed with the change of pH in washing solution to find out the pH range having high removal efficiency of heavy metal. Washing solution was titrated with the addition of HCl or NaOH solution (0.1 M) in distilled water and total 6 kinds of pH conditions (pH 1, 3, 4, 6, 9 and 11) were applied for the experiment. S4 soil sample was sieved with larger than 0.297 mm in diameter. Fifteen grams of soil was mixed with washing solution (the mass ratio of soil to washing solution was 1:1) in 100 ml flask, which was shaken at 180 rpm and 20 °C for 1 hour. After washing, the supernatant in the flask was filtered by 5B filter paper and was analyzed on ICP/OES for As, Pb and Cu concentration. Total amount of heavy metal (As, Pb and Cu) extracted from soil and their removal efficiencies (%) were calculated from the discrepancy of heavy metal concentrations in washing solution between before and after washing process (See Equation 1).

$$\text{Removal efficiency (\%)} = \left(\frac{Initial\ Concentration - final\ concentration}{Initial\ Concentration}\right) \times 100 \quad \text{(Equation 1)}$$

4.2.4 The calculation of remediation goal for each heavy metals

Remediation goal for each heavy metal in washing process was calculated from the discrepancy of heavy metal concentrations between before washing process and KSPWL (Korea soil pollution warning limit) (See Equation 2). The remediation goal of each heavy metal is shown in Table 6.

$$\text{Remediation goal (\%)} = \left(\frac{C_b - KSPWL}{C_b}\right) \times 100 \quad \text{(Equation 2)}$$

where,

C_b = the concentration before the soil washing and KSPWL = Korea Soil Pollution warning limit.

Table 1. Remediation goal of heavy metals for the in experiments

Type of heavy metal	**KSPWL for 1 area (mg/kg)**	**Remediation goal (%)**
Cu	150	94.37
Pb	200	83.74
Cd	4	70.22
As	25	89.95

4.2.5. Batch experiments with various washing solution having different concentration

The extraction efficiency of the soil washing can be increased by using inorganic (e.g., HCl, H_2SO_4, HNO_3 and NaOH) or organic extracts (e.g., citrate, EDTA and oxalic acid) (Bassi et al., 2000; Wassy et al., 2001). In this study, hydrogen chloride (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) solutions were used as the washing solution for the heavy metal removal from S4 soil. Three different concentrations of washing solution (0.05 M, 0.1 M and 0.5 M) were prepared and three different ratios of soil to washing solution (1:1, 1:3 and 1:5) were applied in the experiment to decide the optimal washing condition. A fifteen gram of soil samples was mixed with 15 ml, 45 ml and 75 ml, respectively of each solution. The mixed solution in the flask was shaken at 180 rpm and 20 °C for 30 minute or 1 hour. After washing, the supernatant in the flask was filtered by 5B filter paper and As, Pb and Cu concentration of the solution was analyzed on ICP/OES.

Because of low removal efficiencies of heavy metal, for one time washing, the consecutive washing process was performed to reach the remediation goal. The soil was consecutively washed six times with the fresh washing solution and the removal efficiency was calculated for each washing time. 0.5 M HNO_3 and HCl solutions were used and 15 ml, 45 ml and 75 ml of solution were mixed with 15 g of soil in the flask. After 30 minute of washing, the washed soil was separated from the washing solution. And then, the separated soil was reused for the next soil washing and the accumulative removal efficiency with the increase of recycling times was measured to decide the optimal number of washing times in the soil washing process. Washing conditions of the experiment were the same as those of the previous batch experiment.

Chapter 5. Results and discussion

5.1 Results of soil characterization

5.1.1 Heavy metal concentration and pH of soil

Heavy metal concentrations of 7 soil samples around the Jang Hang smelter and KSPWL (Korean soil pollution warning limit) are shown in Table 1. Arsenic concentrations of S2, S3, S4 and S5 soil sample were higher than KSPWL and concentration of lead, copper and cadmium in S3 and S4 soil samples were also higher than KSPWL. Results showed that S3 and S4 soils were mainly contaminated with arsenic, lead, copper and cadmium (Fig. 6). The concentrations of arsenic, lead, copper and cadmium were determined as 655 mg/kg, 965.78 mg/kg, 2,555.5 mg/kg and 13.43 mg/kg, respectively, which were higher than concentrations of KSPWL. S4 soil was used in this experiment because of its highest heavy metal concentration. Average heavy metal concentrations and pH of S4 soil (grain size of S4 soil particle is larger than 297 μm in diameter) are shown in Table 2.

Table 2. Heavy metal concentrations (mg/kg) of 7 soil samples

Soil sample	**As**	**Pb**	**Cu**	**Cd**
S1	212	8.2	20.7	n.d.
S2	242	382.6	363.4	1.5
S3	733	1753.3	3874.4	23.3
S4	655	965.8	2555.3	13.4
S5	86	172.1	121.9	n.d.
S6	53	102.5	84.9	n.d.
S7	23	9.6	97.8	n.d.
*KSPWL	75	600	450	12

*n.d.: < detection limit ; * KSPWL: Korea soil pollution warning limit

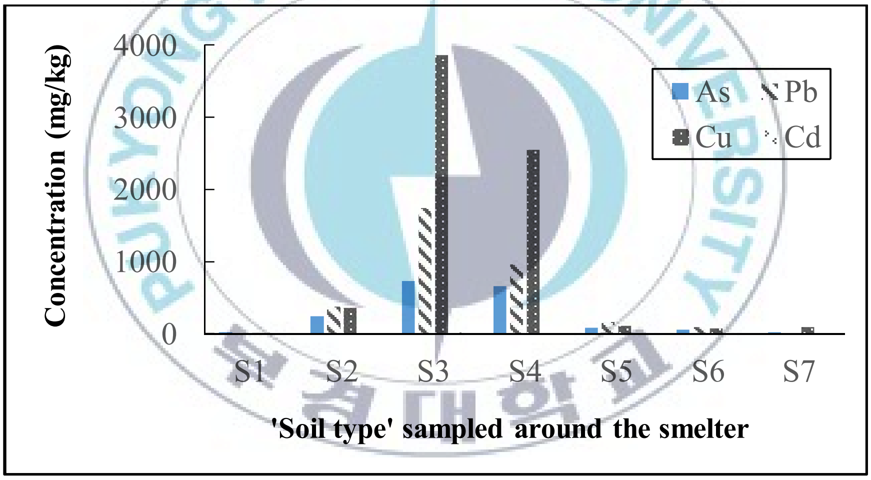


Fig. 6. Results for the heavy metal concentrations of seven soil samples.

Table 3. Average heavy metal concentration (mg/kg) and pH of S4 soil particle (larger than 297 μm in diameter)

Concentration (mg/kg)				
As	Cu	Pb	Cd	pH
248.6	2666.8	1229.9	13.4	5

5.1.2 Physicochemical properties of soil

Results of grain size analysis for the S4 soil sample are shown in Table 3. To decide 'soil texture', the result was plotted on the soil textural triangle from the United States Department of Agriculture (USDA) (Fig. 7). According to the analytical results, more than 99 % of S4 soil was composed of "sand", particle and less than 1 % was "silt and clay" particle. Soil texture of S4 soil was classified as "Sand", suggesting that the major grain size of S4 soil ranged between 300-425 μm in diameter. When the proportion of fine grains in a soil was small, the soil washing process may be further simplified because the additional separation process can be eliminated in washing process. It was investigated that S4 soil was appropriate for the soil washing because the percentage of its fine grains (silt and clay) was significantly low (<1 %).

Table 4. Result of grain size analysis for S4 soil

Gravel particle type	Mesh size	Weight of the soil (g)	Mass ratio (%)
	4.76 mm	6.1	2.03
Sand	2 mm	59.35	19.78
	841 μm	102.5	34.16
	420 μm	91.02	30.34
	297μm	32.97	10.99
	250 μm	3.3	1.1
	149 μm	1.22	0.41
	74 μm	1.04	0.36
Silt and Clay	< 75 μm	2.5	0.83
	Total	**300**	**100**

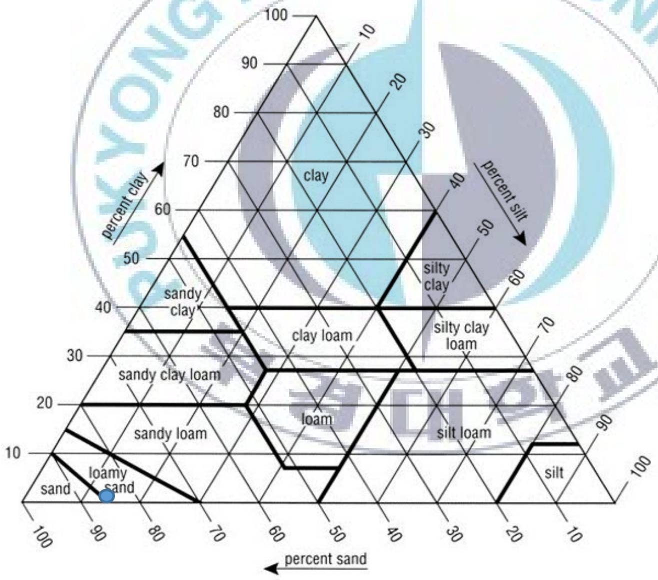


Fig. 7. Soil textural class of soil S4 ( ). ●

5.1.3 Determination of the cut-off size for the soil washing

It is necessary to decide the domain of grain size for the soil washing to get the high concentration of heavy metal. Particles of soil S4 were divided into 8 sub-groups according to their sizes for the cut-off size of the soil washing. Result of grain size distribution ratio, concentration of heavy metal and mass of ratio (% wt) of grains belong to each sub-group are shown in Table 4. For the sub-groups (> 2 mm in diameter), arsenic, copper, lead and cadmium concentration was 183 mg/kg, 1,454 mg/kg, 780 mg/kg and 29 mg/kg, respectively. For the sub-group (>841 µm in diameter), arsenic, copper, lead and cadmium concentration were 321 mg/kg, 1,474 mg/kg, 1,465 mg/kg and 33 mg/kg, respectively. For the sub-group (> 420 µm), arsenic, copper, lead and cadmium concentration was 456 mg/kg, 1,810 mg/kg, 2,109 mg/kg and 33 mg/kg, respectively. For the particles (> 297 µm), arsenic, copper, lead and cadmium concentration was 439 mg/kg, 2,209 mg/kg, 1,446 mg/kg and 33 mg/kg, respectively. For larger than 250 µm; arsenic, copper, lead and cadmium concentration was 716 mg/kg, 2,290 mg/kg, 1,432 mg/kg and

33 mg/kg, respectively. For > 149 μm; arsenic, copper, lead and cadmium concentration was 706 mg/kg, 2,597 mg/kg, 1,754 mg/kg and 33 mg/kg, respectively. For less than 149 μm arsenic, copper, lead and cadmium concentration was 584 mg/kg, 2,278 mg/kg, 1,296 mg/kg, 1,296 mg/kg and 33 mg/kg, respectively. Heavy metal concentrations of soil particles increased with the decrease of grain size. From the analysis, the particle size for the washing in this experiment was determined as the range of 4.76 mm and 297 μm. In this study, the soil whose size is larger than 297 μm was chosen for the soil washing process because coarse grained particles (> 297 μm) contained high heavy metals and also covered more than 95.27 % of total soil particles. The soil washing process for fine grains (clay and silts) is not available because their heavy metal removal efficiencies were low.

Table 5. Sub groups of particles for the cut-off size of S4 soil

Sub-group #	Mesh size of grain (diameter:µm)	Contamination (mg/kg) As	Cu	Pb	Proportion of particle (wt %)
1	**4 (4.76 mm)**	398	1,730	1,715	2.03
2	**10 (2 mm)**	183	1,454	780	19.78
3	**20 (841 µm)**	321	1,474	1,465	34.16
4	**40 (420 µm)**	456	1,810	2,109	30.34
5	**50 (297µm)**	440	2,209	1,446	10.99
6	**60 (250 µm)**	716	2,290	1,432	1.1
7	**100 (149 µm)**	706	2,597	1,754	0.41
8	**200 (74 µm)**	584	2,278	1,296	0.36

5.2. Results of batch experiment

5.2.1. Batch experiments for soil washing with various pH conditions

Soil washing of S4 soil with various pH of solution was performed to decide the optimal pH range of washing solution to achieve the high removal efficiency of arsenic, lead and copper. Copper and lead removal efficiencies for pH 1 solution were 14.45 % and 7.20 % at 1:1 ratio of contaminated soil to washing solution for 1 hour (Fig. 8). Form the, it is necessary for washing with strong acidic solution lower than pH 1, with strong basic solution higher than pH 11, or with additional reagents.

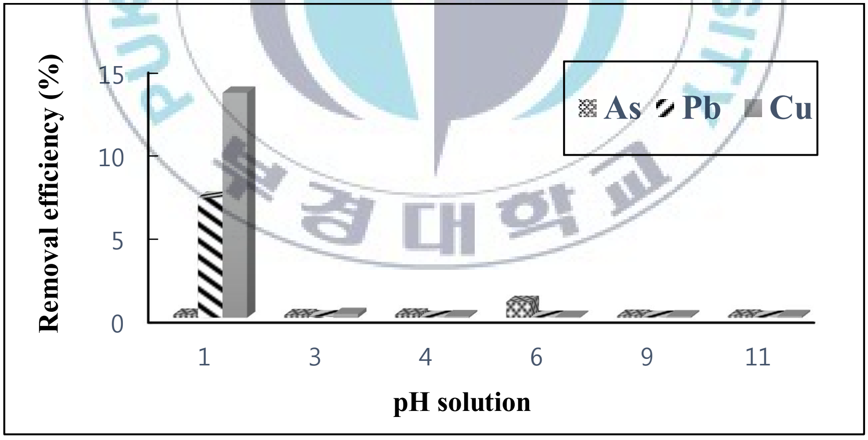
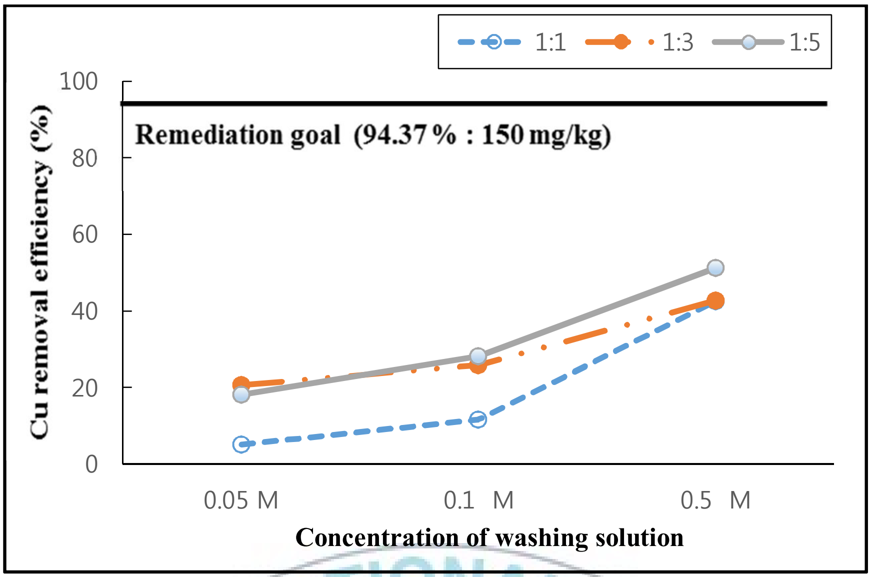


Fig. 8. Removal efficiencies of the soil washing with various pH of solution.

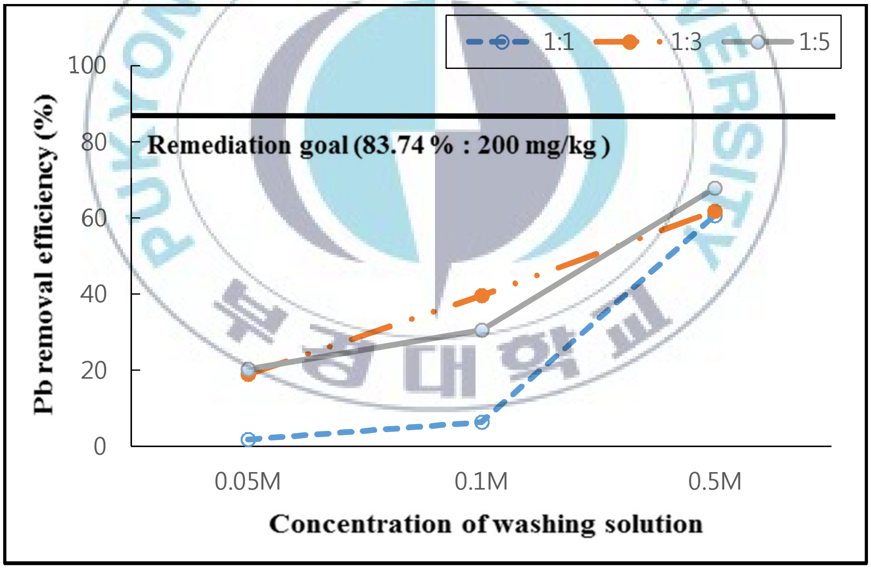
5.2.2. Batch experiments with various washing solution

5.2.2.1. Batch experiment with HNO_3 solution

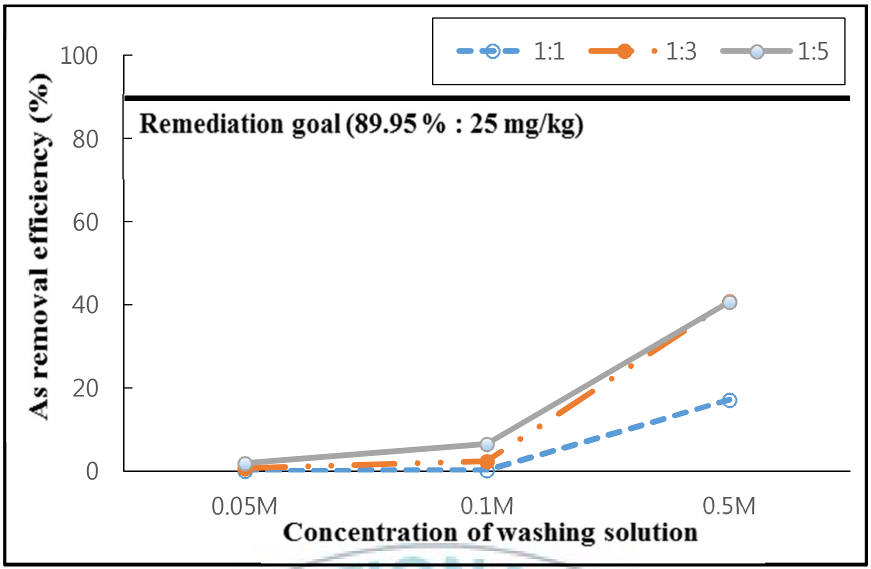
Results of the washing experiment with HNO_3 solution are shown in Fig. 9. Removal efficiency increased with the increase of concentration of HNO_3 in solution and the ratio of soil to washing solution. Removal efficiency of copper was 20.62 % when 0.05 M of HNO_3 solution was used (Fig. 9 (a)). And it maintained at an average of 14.63 % regardless of the ratio of soil to solution. Lead removal efficiency was 63.40 % with 0.5 M of HNO_3 solution for 30 minute washing. Removal efficiency of lead decreased as 13.68 % when 0.05M solution was used (Fig. 9 (b)). Removal efficiency of arsenic was 0.85 % when 0.05 M solution was used and the removal efficiency increased up to 32.85 % when 0.5 M solution was used (Fig. 9 (c)). Despite using of 0.5 M of HNO_3 as washing solution the removal efficiency of heavy metal was lower than the remediation goal (KSPWL: Korean soil pollution warning limit)


1:1
1:3
1:5
Cu removal efficiency (%)
100
80
60
40
20
0
Remediation goal (94.37 % : 150 mg/kg)
0.05 M
0.1 M
0.5 M
Concentration of washing solution

(a) Cu


1:1
1:3
1:5
Pb removal efficiency (%)
100
80
60
40
20
0
Remediation goal (83.74 % : 200 mg/kg)
0.05M
0.1M
0.5M
Concentration of washing solution

(b) Pb

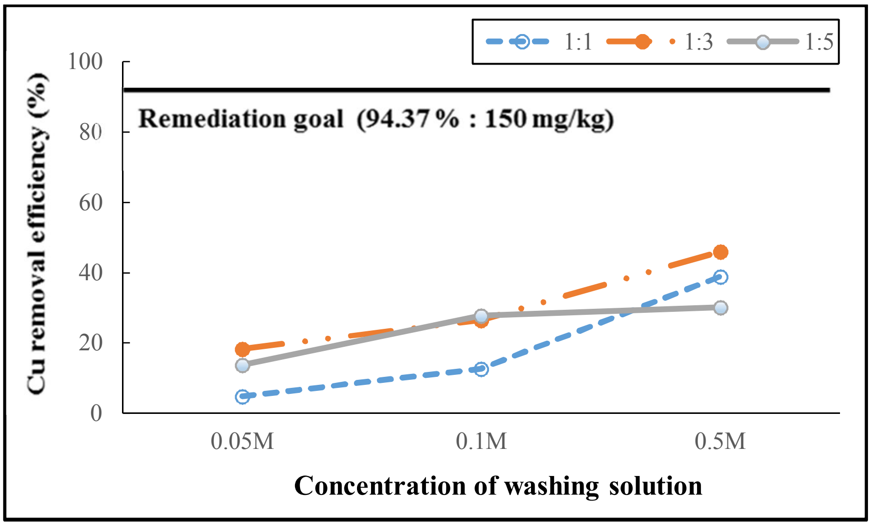


(c) As

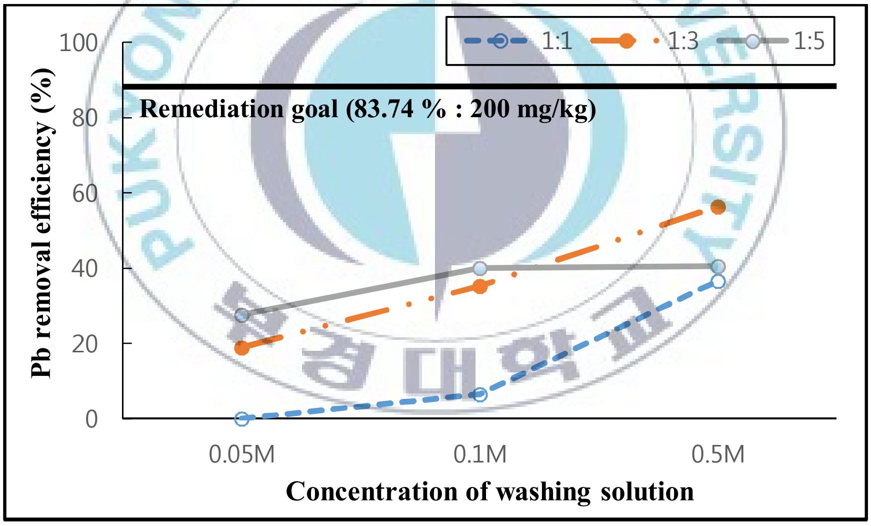
Fig. 9. Result of heavy metal removals for 30 minute washing with HNO_3 solution.

5.2.2.2 Batch experiments with HCl solution

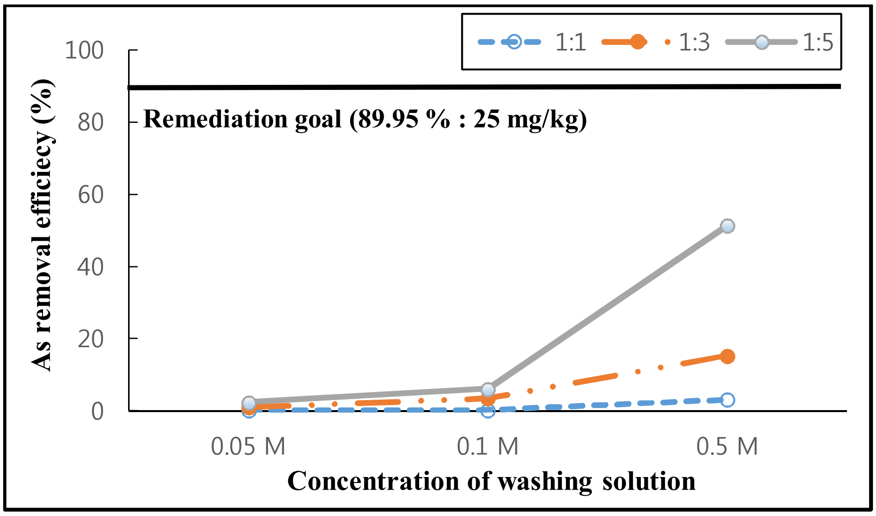
Removal efficiency of copper was determined as 18.40 % at 1:3 ratio of soil to 0.05 M of HCl solution. Removal efficiency of copper at 1:3 ratio of soil to 0.5 M of HCl solution was determined as 46.12 %, which was the highest removal efficiency of copper. As the result, the washing condition with 1:3 ratio of soil to washing solution was effective to remove copper from S4 soil (Fig. 10 (a)). Removal efficiency of lead was 19.03 % when 0.05 M solution was used and the removal efficiency increased to 56.43 % when 0.5 M solution was used (Fig. 10 (b)). Removal efficiency of arsenic was 1 % when 0.05 M solution was used and the removal efficiency increased to 15.24 % when 0.5 M solution was used (Fig. 10 (c)). In the case of HCl solution, the removal efficiency of lead was higher than those of other heavy metals. In the case of using HCl solution, in common with the case of using HNO_3 solution, the removal efficiency was lower than the remediation goal, therefore, the consecutive washing might be required.


1:1
1:3
1:5
100
80
60
40
20
0
Remediation goal (94.37 % : 150 mg/kg)
Cu removal efficiency (%)
0.05M
0.1M
0.5M
Concentration of washing solution

(a) Cu


1:1
1:3
1:5
100
80
60
40
20
0
Remediation goal (83.74 % : 200 mg/kg)
Pb removal efficiency (%)
0.05M
0.1M
0.5M
Concentration of washing solution

(b) Pb

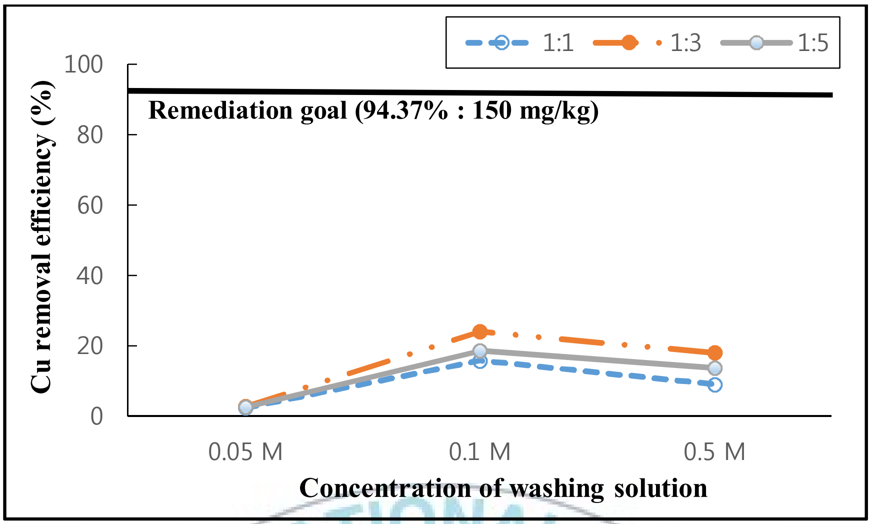


(c) As

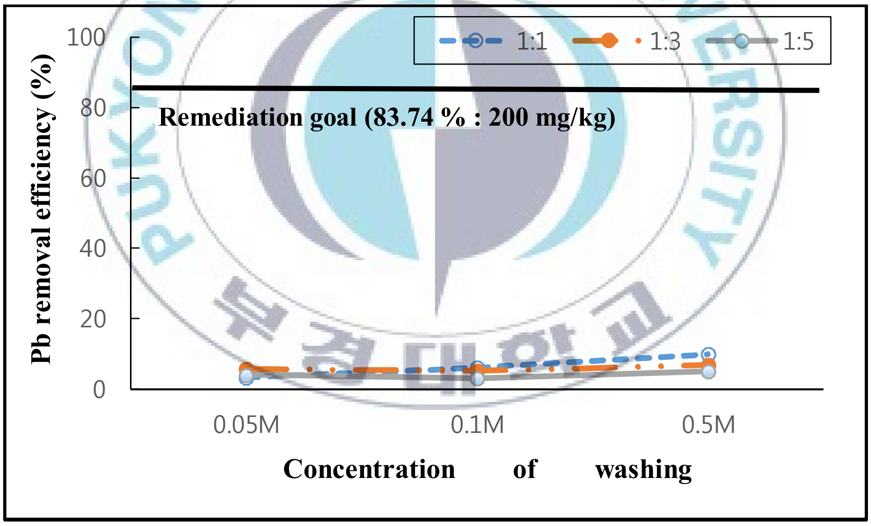
Fig.10. Result of heavy metal removals for 30 minute washing with HCl solution.

5.2.2.3 Batch experiments with H_2SO_4 solution

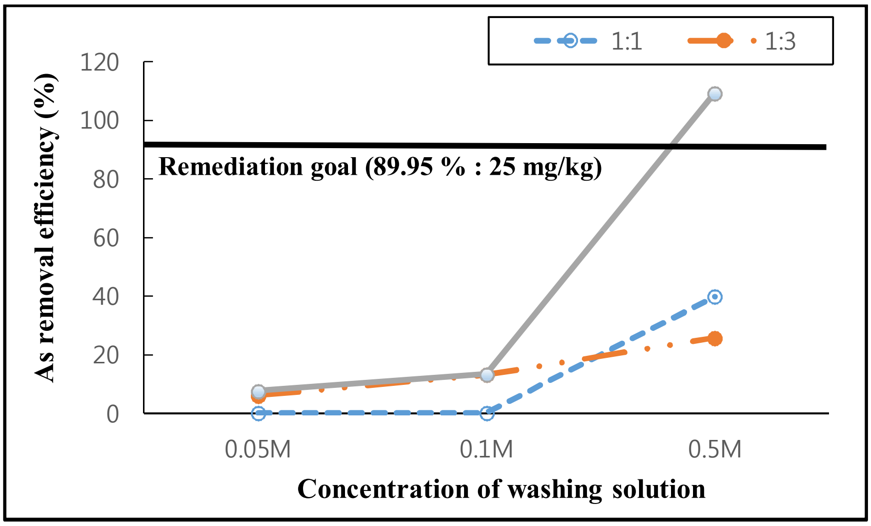
From the batch experiments using H_2SO_4 washing solution, the removal efficiency of copper was determined as 18 % at 1:3 ratio of soil to 0.05 M of H_2SO_4 solution. When the washing condition was 0.1 M of H_2SO_4 solution, copper removal efficiency increased to as 24 %, which was the highest removal efficiency of copper. But, all removal efficiencies of copper were lower than the remediation goal (94.37 %) (Fig. 11 (a)). The highest removal efficiency of lead was 9.88 % at 1:1 ratio of soil to 0.5 M of H_2SO_4 solution, which was less than 10 %, suggested that H_2SO_4 solution was not effective to remove lead from S4 soil (Fig. 11 (b)). The removal efficiency of arsenic was over 100 % at 1:5 ratio of soil to 0.5 M of H_2SO_4 solution, which was higher than the remediation goal (89.95 %) (Fig. 11 (c)). In the case of arsenic, the removal efficiencies by using H_2SO_4 washing solution were higher than those by using HNO_3, HCl and NaOH washing solution for 30 minute washing. One time washing was not effective to remove all heavy metals. Therefore, the repeated washing would be better to remove heavy metals from S4 soil.


1:1
1:3
1:5
100
80
60
40
20
0
Cu removal efficiency (%)
Remediation goal (94.37% : 150 mg/kg)
0.05 M
0.1 M
0.5 M
Concentration of washing solution

(a) Cu


1:1
1:3
1:5
100
80
60
40
20
0
Pb removal efficiency (%)
Remediation goal (83.74 % : 200 mg/kg)
0.05M
0.1M
0.5M
Concentration of washing

(b) Pb

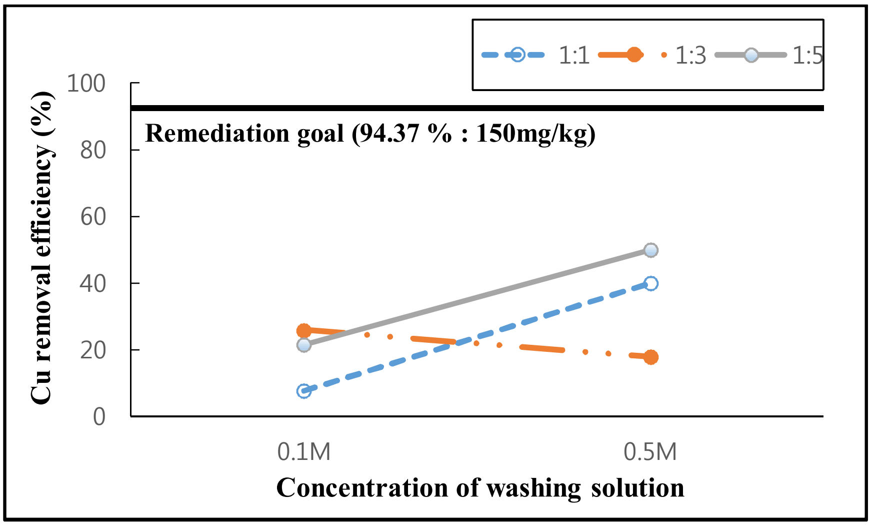


(c) As

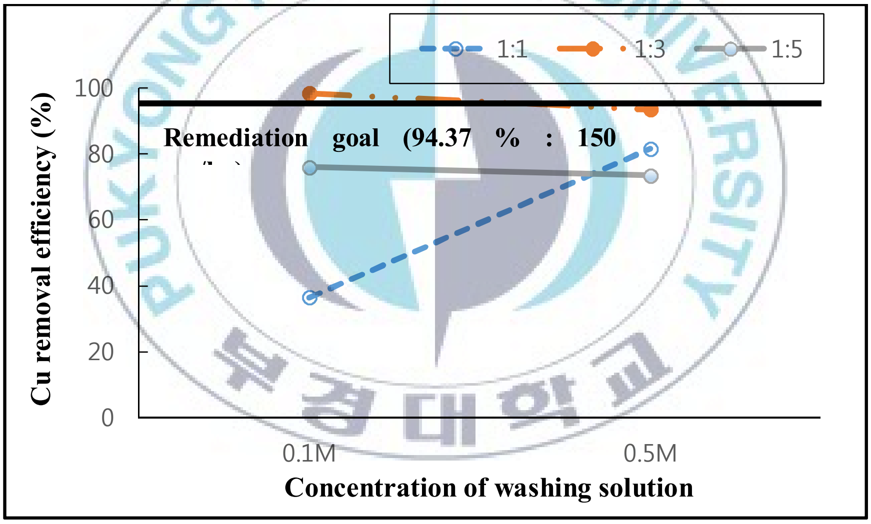
Fig.11. Result of heavy metal removals for 30 minute washing with H_2SO_4 solution.

5.2.2.4 Batch experiment with NaOH solution

During the experiment, the removal efficiency of 1 hour washing process was higher than 30 minute washing process when NaOH washing solution was used. The removal efficiency of copper was 98.32 % at 1:3 ratio of soil to 0.1 M of NaOH solution for 1 hour, which was higher than the remediation goal (94.37 %) (Fig. 12). The highest removal efficiency of lead was 71.47 % at 1:3 ratio of soil to 0.1 M of NaOH solution for 1 hour washing (Fig. 13). Removal efficiency of arsenic reached to the remediation goal at 1:3 ratio of soil to 0.5 M of NaOH solution at only 1 hour washing. Removal efficiency increased with the increase of washing time (from 30 minute to 1 hour) and concentration of washing solution. The removal efficiencies of (Fig. 12 and Fig 14) reached to the remediation goal at 1:3 ratio of soil to solution for 1 hour washing (98.32 % and 92.18 %, respectively). On the contrary, the removal efficiency of lead did not reach to the remediation goal at all washing condition. However, the removal efficiencies of heavy metals by using NaOH washing solution were higher than those by using HNO_3, HCl and H_2SO_4 washing solution.

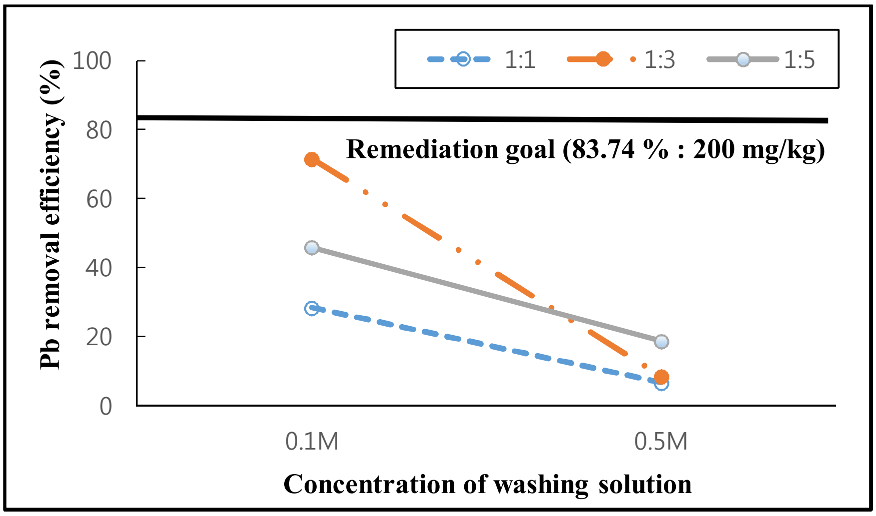


(a) 30 minute washing



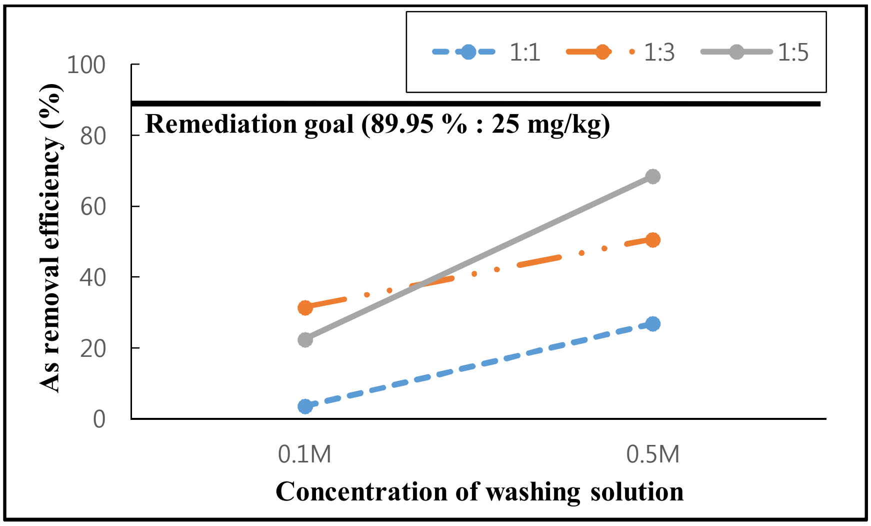
(b) 1 hour washing

Fig. 12. Cu removal efficiency for 30 minute and 1 hour washing with NaOH solution.

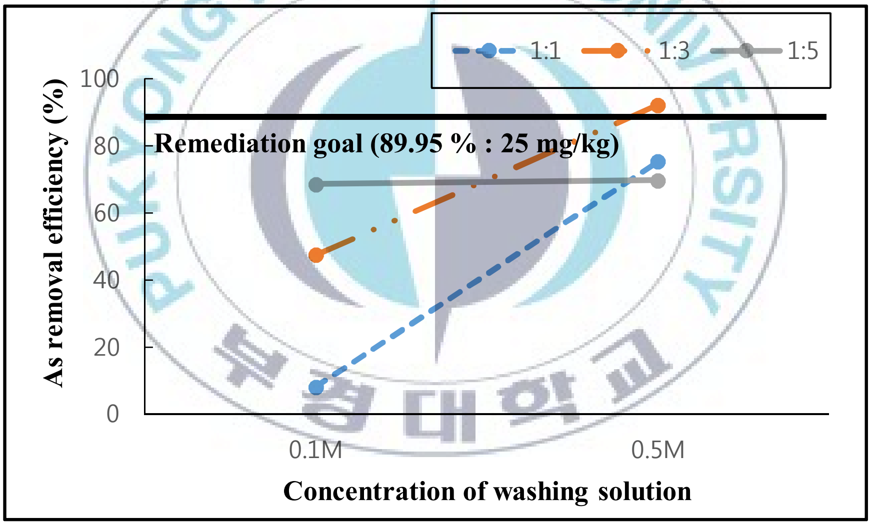


a) 1 hour washing

Fig.13. Pb removal efficiency for 1 hour washing with NaOH solution.



(a) 30 minute washing



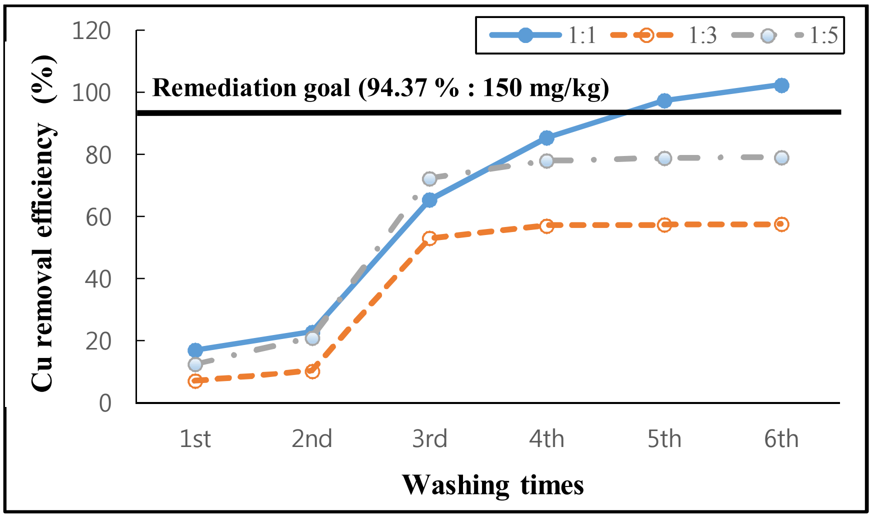
(b) 1 hour washing

Fig. 14. As removal efficiency for 30 minute and 1 hour washing with NaOH solution.

5.2.3. Batch experiments with the repeated washing

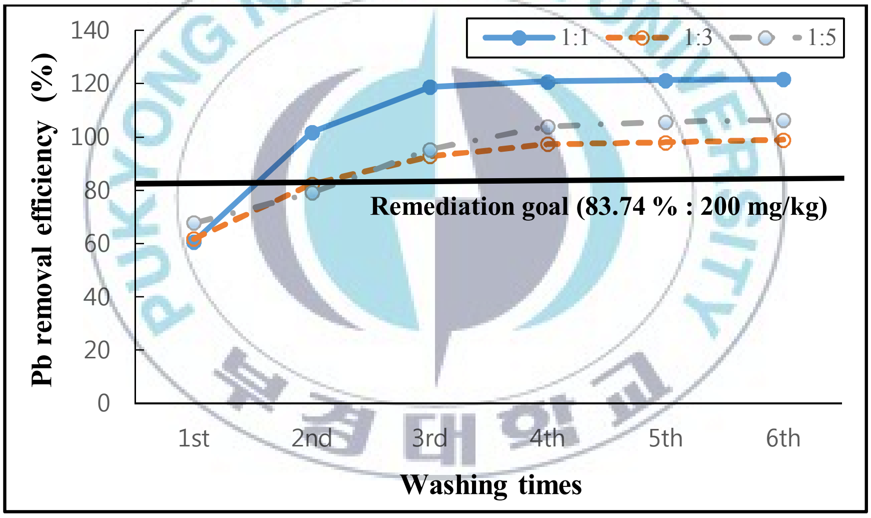
5.2.3.1. Copper, lead and arsenic removal efficiencies with HNO_3 solution

The accumulative removal efficiency (%) for six consecutive washings with 0.5 M of HNO_3 solution is shown in Fig. 15. The washing time was 30 minute and the ratio of soil to solution was 1:1, 1:3 and 1:5 in the experiment. From the results, removal efficiencies of copper, lead and arsenic increased with the increase of the repeated washing times. The accumulative removal efficiency of copper maintained more than 97 % after the 5th washing (Fig. 15 (a)). The accumulative removal efficiency of lead was over than 100 % at 1:1 ratio soil to solution after the 2nd washing and it reached the remediation goal at 1:3 and 1:5 ratio of soil to solution after the 3rd washing (92.7 % and 95.3 %, respectively) (Fig. 15 (b)). On the contrary, the accumulative removal efficiency of arsenic did not reach to the remediation goal at all repeated washing experiments. (Fig. 15 (c)). From these results, suggesting that the lead and copper can be successfully removed by 5 repeated washing with HNO_3 solution.



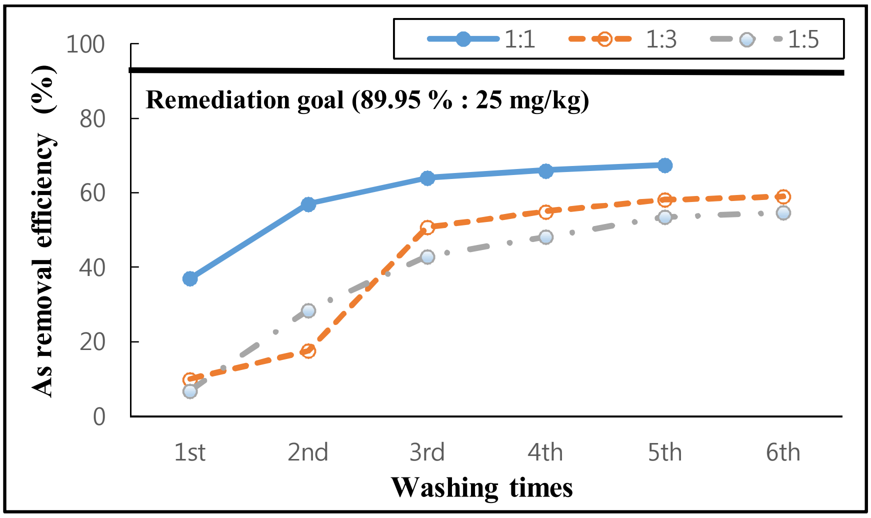
1:1
1:3
1:5
Remediation goal (94.37 % : 150 mg/kg)
Cu removal efficiency (%)
120
100
80
60
40
20
0
1st
2nd
3rd
4th
5th
6th
Washing times

(a) Cu



1:1
1:3
1:5
Remediation goal (83.74 % : 200 mg/kg)
Pb removal efficiency (%)
140
120
100
80
60
40
20
0
1st
2nd
3rd
4th
5th
6th
Washing times

(b) Pb

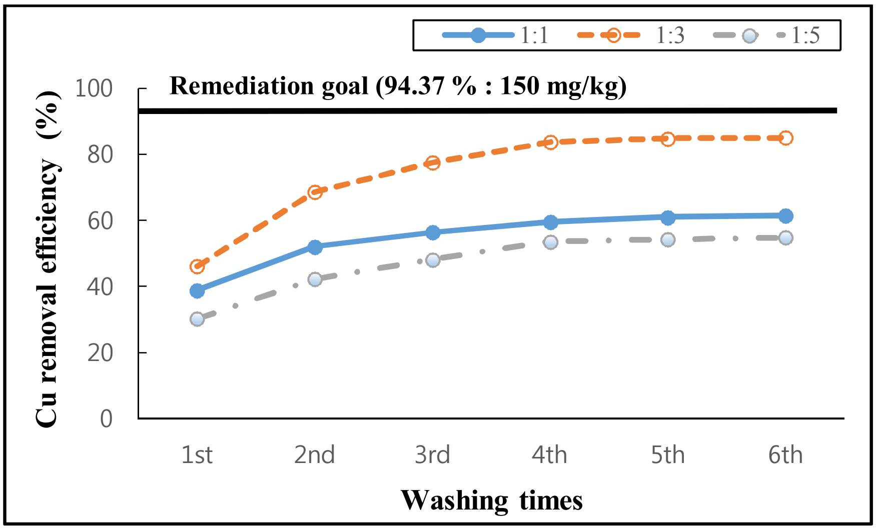


(c) As

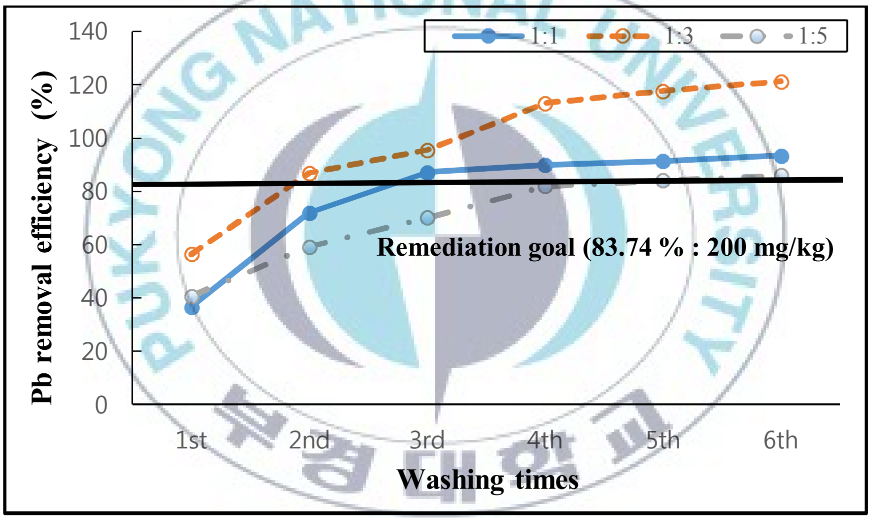
Fig. 15. Result of heavy metal removal efficiencies for 6 consecutive washing with HNO_3 solution.

5.2.3.2 Copper, lead and arsenic removal efficiencies with HCl solution

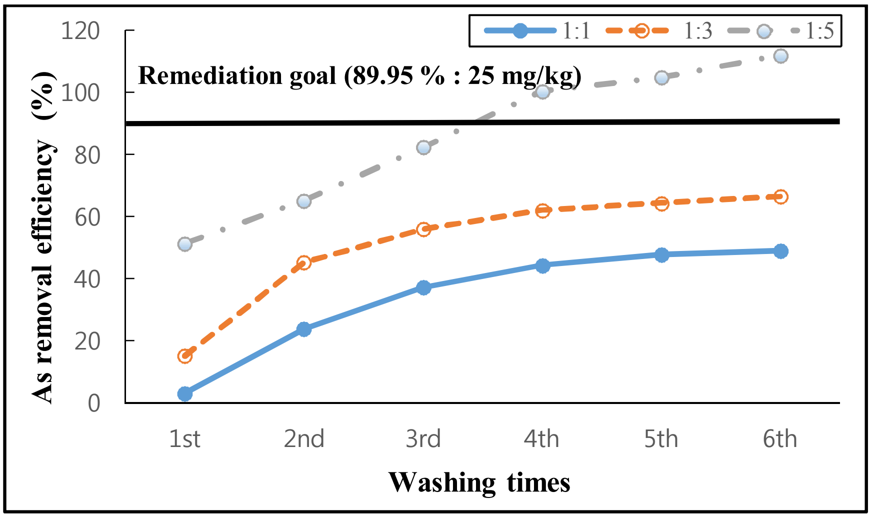
The accumulative removal efficiency of six consecutive washings with 0.5 M of HCl solution are shown in Fig. 16. The washing time was 30 minute and the ratio of soil to solution was 1:1, 1:3 and 1:5 in the experiment. From results, the removal efficiencies of copper, lead and arsenic increased with the increase of the consecutive washing times. The removal efficiency of copper did not reach to the remediation goal after six washing times (Fig. 16 (a)). For the lead, higher than the remediation goal the highest removal efficiency was at 1:3 ratio of soil to solution after the 2nd washing (Fig. 16 (b)). The removal efficiency of arsenic were over than 100 % only at 1:5 ratio of soil to solution after 4th washing (Fig. 16 (c)).


1:1
1:3
1:5
Remediation goal (94.37 % : 150 mg/kg)
Cu removal efficiency (%)
100
80
60
40
20
0
1st
2nd
3rd
4th
5th
6th
Washing times

(a) Cu


1:1
1:3
1:5
Remediation goal (83.74 % : 200 mg/kg)
Pb removal efficiency (%)
140
120
100
80
60
40
20
0
1st
2nd
3rd
4th
5th
6th
Washing times

(b) Pb



(c) As

Fig. 16. Result of heavy metal removal efficiencies for six consecutive washings with HCl solution.

Chapter 6. Conclusion

Feasibility of soil washing for the remediation of heavy metal contaminated soils around the Jang Hang smelter was evaluated through the batch experiment. The following conclusions are achieved from this research.

1. Copper, lead and arsenic contaminated soil samples were collected around the Jang Hang smelter, Korea. From the results of aqua regia extraction process, copper, lead and arsenic concentrations in S4 soil were 2,667 mg/kg, 1,230 mg/kg, and 249 mg/kg, respectively, suggesting that it was highly contaminated by heavy metals.

2. More than 99 % of particles in S4 soil were belong to 'sand' in soil texture analysis. The have used cut-off size of the soil particle diameter for at the soil washing was determined as the range from 4.76 mm to 0.297 mm. They covered more than 95.27 % of total soil particles and were also contaminated by heavy metals

3. For the batch experiment with 0.5M of HNO_3 solution at 1:1, 1:3 and 1:5 ratio of soil to washing solution

for 30 minute washing, the highest removal efficiency of copper was 51 % and 68 % for lead, suggesting that it is possible to remediate S4 soil by the consecutive washing process with HNO_3 solution.

4. For the batch experiment with 0.5 M of HCl solution at 1:1, 1:3 and 1:5 ratio of soil to washing solution for 30 minute washing, the highest removal efficiency of copper and lead were 46 % and 56 %, respectively. For the arsenic, the highest removal efficiency was 51 % at 1:5 ratio of soil to washing solution, suggesting that it is possible to remediate S4 soil by the consecutive washing process with HCl solution.

5. For the batch experiment with 0.1 M and 0.5 M of NaOH at 1:3 ratio of soil to washing solution for 1 hour washing, the highest removal efficiency of copper and arsenic were 98 % and 92 %, respectively, suggesting that the optimal washing solution was NaOH solution for the copper and arsenic. However, the removal efficiency of lead for NaOH solution was lower than the remediation goal, and the repeated washing or the use of additional washing solution are needed for S4 soil remediation.

6. For the six repeated washing with 0.5 M of HNO_3 solution, the removal efficiencies of copper and lead after the 5th washing were higher than the remediation goals. Removal efficiency of lead was over than 100 % at 1:1 ratio soil to solution after the 2nd washing and it reached the remediation goal at 1:3 and 1:5 ratio of soil to solution after the 3rd washing (93 % and 95 %, respectively) with HNO_3. For 0.5 M of HCl solution, the removal efficiency of lead after the 2rd washing was higher than the remediation goal. For the lead, higher than the remediation goal the highest removal efficiency was at 1:3 ratio of soil to solution after the 2nd washing with HCl solution.

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The finally, based on the all results and the properties of the soil, the optimal soil washing condition was suggested to remove heavy metals from soil around of the Jang Hang smelter. It was 1:3 ratio of soil to 0.1 M of NaOH solution for 1 hour.

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Contaminated Soil around Abandoned Mines.

장항제련소 주변 중금속 오염토양 복원을 위한 토양세척법 적용

Enkhzaya Choijilsuren

부경대학교 대학원 지구환경과학과

요약문

충청남도 장항제련소 주변 중금속으로 오염된 토양내 중금속 제거하는 토양세척법의 효율성을 규명하기 위한 실내 배치실험을 수행하였다. 제련소주변에서 채취한 총 7가지 토양시료 중 가장 오염도가 높은 S4 토양의 구리, 납, 비소 농도 각각 2,667mg/kg, 1,230 mg/kg, 249 mg/kg 으로 나타나, 1지역 토양오염기준(Cu:450 mg/kg, Pb mg/kg, As: 75 mg/kg) 초과하는 것으로 나타났다. 오염토양부터 중금속을 제거하기 위하여 세척액 종류(염산, 질산, 황산, 수산화나트륨) 농도(0.05M, 0.1M, 0.5M), 오염토양과 세척액의 비율(1:1, 1:3, 1:5), 세척시간(30분, 60분)을 달리하여 토양세척 배치실험을 수하였다. 토양세척 실험을 실시한 결과, 수산화나트륨 용액을 이용해 1시간 동안 세척하였을 때 0.1M 와 0.5M 용액을 사용하는 경우, 구리, 납, 비소의 제거효율이 70%를 효과하였다, 질산과 염산으로 30분 동안 세척하였을 때 제거효율이 60% 이상으로 나타났다.

황산 용액의 경우에는 30% 이하의 낮은 제거효율은 나타냈다. 이 결과에 따라 수산화나트륨 세척용액이 장항제련소 주변 토양의 중금속을 제거할 때 다른 용액 보다 더 효과가 좋은 것으로 나타났다. S4토양을 수산화나트륨 0.5M 용액을 이용하여,1:3 비율로, 1시간 세척 하였을 때, 납과 구리의 제거 효율은 각각 93%, 92%로 나타났다. 질산 0.5M 용액을 1:5의 비율로 30분 동안 세척한 경우 구리, 납, 비소의 제거효율은 각각 51%, 68%, 40%로 나타났다. 염산 0.5M 용액을 1:3 비율로 이용하였을 경우 구리, 납의 제거 효율이 각각 46%와 56%로 나타났고, 비소는 1:5 비율로 세척한 경우 제거효율이 51% 나타났다.

1회 세척으로 중금속 제거효율이 제거 복표 (KSPWL: 한국토양오염우려 기준)에 도달하지 않았기 때문에, 실험 결과 따라 염산과 질산 0.5M 용액을 이용하여 6번 연속 세척을 실시했다. 실험 결과 질산 용액을 이용해 1:1 비율로 5회 세척 하였을 때 구리의 누적 제거효율은 97%으로 제거목표에 도달하였고, 납의 누적 제거 효율은 1:1 비율로 2회 세척 후 100% 이상으로 제거목표에 도달하였다. 염산용액을 1:3 비율로 2회 세척 후 납의 제거효율은 86%로 제거목표에 도달하였고, 1:5 비율로 4회 세척 후 비소의 제거효율은 100% 이상을 나타내였다.

실내 실험 결과로부터 따라 장항제련소 주변 오염토양 대하여 수산화나트륨 0.1M 용액을 이용하여 1:3 비율로 1시간 이상 세척을 수행한다면, 구리, 납, 비소 모두 제거목표에 도달할 것으로 기대된다.

주제어 : 장항제련소, 중금속오염, 토양세척법

감사 글

2년 전에 처음 한국에 왔을 때에는 지구환경학에 대해 아무것도 모르고 왔었다. 아무것도 모르는 백지 같은 저에게 지구환경이라는게 뭔지를 알려주신 지구환경과학 교수님들께 진심으로 감사의 마음을 전하고 싶다. 순식간에 지나간 2년동안 따뜻한 마음으로 우리 아버지처럼 대해주시고 나 때문에 고생도 많이 하시고 그래도 끝까지 기대해주면서 지도해주신 이민희 교수님께 진심으로 감사드립니다. 그리고 지구환경 다니는 동안 저한데 여러가지로 도움을 주시고 또 많은 것을 알려주신 박맹언, 황덕흥 , 김염석, 최정장 교수님들에게 진심으로 감사드립니다. 또는 그동안 환토방이라고 가족을 만들고 울었을 때 같이 울고, 웃었을 때 같이 웃어주며 항상 곁에 있어줬던 우리 어머니 같은 분이신 이경박사님, 큰 언니 상희언니, 우리 착한 방장 수민이, 재미있고 무섭고 명랑한 효진이, 내 친오빠를 상기시킨 세윤이, 언제나 같이 있으며 쾌활한 정택이, 말수가 적은 원지, 신중한 우리 막내 아름이, 익살스러운 승헌이 그리고 하전이, 경배 선배님들, 주언이 또 항상 밥 칭겨준 우리 영주에게 진심으로 감사의 말을 전합니다. 선배들과 친구들이 없었으면

타지에 온 제가 무사히 졸업을 못했을 것 같다. 짧은 시간있었지만 제 생에 그리워할 깊은 추억들이 남겨진 시간이었다. 마지막으로 사랑한 부모님, Sukhee 오빠, 또 Uugantsegtseg 언니 그리고 박종진 명예영사님에게 정말로 감사합니다. 앞으로도 저는 여러분의 믿음을 간직하고 살아갈 것입니다.