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공학석사 학위논문

Physico – Chemico and Thermally
Enhanced Soil Washing
for Heavy Metal Contaminated Site
at Yongsan Railroad Area

용산 철도부지 중금속 오염토양 정화를 위하여 물리적,
화학적, 열적으로 개선된
토양세척 연구

2017년 2월

서울대학교 대학원

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이 논문을 공학석사 학위논문으로 제출함
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Abstract

Physico - Chemico and Thermally Enhanced Soil Washing for Heavy Metal Contaminated Site at Yongsan Railroad Area

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A series of soil washing tests was conducted on railroad site soil with high concentration of copper (Cu), lead (Pb), and zinc (Zn). The initial heavy metal concentration of soil was varied from 1069 mg/kg to 2870 mg/kg for Cu, 873 mg/kg to 3300 mg/kg for Pb, and 279 mg/kg to 829 mg/kg for Zn. Since the soil was heavily contaminated, optimization and enhancement for soil washing was needed. In this study, enhancement performance of soil was conducted based on optimization in chemical aspect and addition of physical and thermal effect in the system. It was found that the proper condition in chemical aspects was using sequential washing by 0.2 M Na₂-EDTA solution followed by 0.5 M HCl, 1:5 g/ml of solid liquid ratio, and 30 minutes of contact time. In addition, physical effect affected in breakage soil aggregation, which was found effectively enhance the performance by changing stirring speed to 120 rpm and using dispersing agent 2% in this experiment. Furthermore, more increment of removal efficiency occurred by increasing temperature up to 70 °C because it favoured molecular movement and collision between contaminant and washing solution. Nevertheless raising

higher temperature would decrease in performance for Cu. Compared to conventional chemically soil washing only, adding physical and thermal effect into the system will enhance performance from 30.0% to 62.5% for Cu, 53.7% to 79.8% for Pb, and 40.7% to 66.5% for Zn.

Keywords: Soil washing, Railroad contamination, Heavy metal, Physical effect, Chemical effect, Thermal effect

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CHAPTER 1 INTRODUCTION

1.1 Background

Along with the development of technology, there are numerous activities that produce harmful chemicals during and/or after their activities to the environment surrounded. Rail transportation is known as one of them that can create adverse effect to the environment (Masoudi et al. 2012; Li et al. 2001). Many activities from locomotive and engine maintenance, rail ties, spillage and leakage from transportation operations, will result many typical pollutants, such as heavy metals, polyaromatic hydrocarbons (PAH), and polychlorinated byphenils (PCB) (Wilkomirski et al. 2012). Cu, Zn, Cd, and Pb are the typical metal pollutants produced by their traffic activities (Yan et al. 2012; US-Government 2001). According to the U.S. Environmental Protection agency, and the International Agency for Research on Cancer, those heavy metals are classified as human carcinogens (Fergusson 1994). Because of their high degree of toxicity, they are ranked among the priority metals of public health significance. (Tchounwou et al. 2014).

Yongsan area had been used as a railroad marshalling yard and depot since 1905 in Seoul, South Korea and operated until 1980s (Moon et al. 2016; Baek et al. 2012). When the re-development plan was set, this area is found contaminated by oil and heavy metals, both in groundwater and soil. About 388,000 cubic meters of industrial waste is found buried and the extreme concentration is measured 83 times higher than standard limit set by Korean Soil Environment Conservation Act for residential area (Kang, 2013).

Among different types of soil remediation, soil washing is usually performed in railroad contaminated area. There are many kinds of advantage in soil washing method; reducing volume of contaminant, relatively low costs,

the high extraction efficiency and the specificity for heavy metal (Karthika et al. 2016). Soil washing has been gradually enhanced through many different trials. Chemically enhanced soil washing is a common trial to get the goal in field remediation. Furthermore, the term of soil washing is also described as process that involves chemical extraction in some literatures (Dermon et al. 2008; Mulligan et al. 2001; Abumaizar and Smith. 1999). However, in some cases, the removal efficiency is not enough since the various characteristics and long term of contaminated soil has strong affinity and tightly bound with soil (Dove et al. 1992). Same case happened in this study, the long period contaminated soil was used. The contaminants are often strongly and heavily spiked onto the soil particles which lead the low removal efficiency in chemical washing. Consequently, enhancing performance of soil washing is needed to achieve minimal standard of soil regulation in South Korea.

In this study, firstly, the optimization study was performed to obtain the proper condition for chemical washing. The variables of chemical condition are washing solution concentration, solid-liquid ratio, and contact time. Thereafter, enhancement performance in physical aspects was conducted by changing speed of rotator and comparing the use of dispersing agent and manually grinding the soil. The basic concept of enhancement by physical effects is how to break soil aggregation in the since soil in the aggregates form contains closed pore which will hinder for mass transfer from bulk liquid (Peng et al. 2013). As the last step, best conditions in chemical and physical aspects were combined with thermal aspect. Under laboratory conditions, the objectives of this study are to find out the optimized condition for chemical washing, and to investigate the effects of physical and thermal addition in chemically soil washing in order to enhance the performance of removal the heavy metals from the railroad contamination site soil.

1.2 Objective and scope of study

This study discusses the addition of physical and thermal effect in conventional chemically soil washing based method, applied for railroad contamination soil at Yongsan Railroad Area. This area had been contaminated by high concentration of heavy metal for long periods of time. The specific objectives are listed below:

1. Find out the optimal condition in chemical aspect, such as washing solution concentration, solid-liquid ratio, and contact time.
2. Increase removal efficiency of soil washing performance by selecting the proper physical method.
3. Increase removal efficiency of soil washing performance by adding thermal into the system.
4. Discover the increment of removal efficiency by adding physical, chemical, and thermal effect together in the system.
5. Compare the results with Korea's Soil Standard Regulation for the application of the study.

Some limitations are applied and not be discussed in the scope of study, such as:

1. The scope of study is only for soil; groundwater is not included.
2. The results are only representative for soil and condition that used in this experiment; different material and method would make different result.
3. The experiment is limited only with scenario order plan of this experiment.
4. Treatment of wastewater produced is not included in this study.

1.3 Outline

This thesis document is divided into five main parts. Each part has its specific discussion as written below.

Chapter 1. Introduction

Chapter 1 contains background of study, the objective and scope of study with its limitation, and also the organization of this thesis document.

Chapter 2. Literature review

All the information related to this study from books, papers, etc. are described in the second chapter. The idea of this chapter is to provide appropriate, reliable and valid information to support author opinions.

Chapter 3. Material and methods

Chapter 3 contains the information about what kind of materials and method that author used in this study. Therefore, in this chapter general concept and scenario order of experiment are also described.

Chapter 4. Results and Discussion

In this chapter, all the results are presented based on the plot scenario order. All the results are analyzed based on academic information in literature review. Furthermore, the results may be compared with another but similar experiment.

Chapter 5. Conclusion

Summary and conclusions for this study are described in this chapter. Moreover, some recommendations for further study are also presented.

CHAPTER 2 LITERATURE REVIEW

2.1. Soil Washing Technique

Soil washing is one of soil remediation ex-situ methods that effective to treat both organic and inorganic contaminants. At first, it used to be known as physical separation methods, with the basic concept is separating contaminant from excavated soil based on soil's particle size. It relies on a fact that contaminants tend to be associated preferentially with organic matter and fine grained soil particle, such as silt and clay (Sharma and Reddy, 2004). In consequence, this method can reduce the volume of soil requiring final treatment or disposal. Volume reduction is achieved by cleaning the coarse-grained soil fraction and leaving the contaminants in fine-grained fraction and washing fluids (USEPA, 1996d).

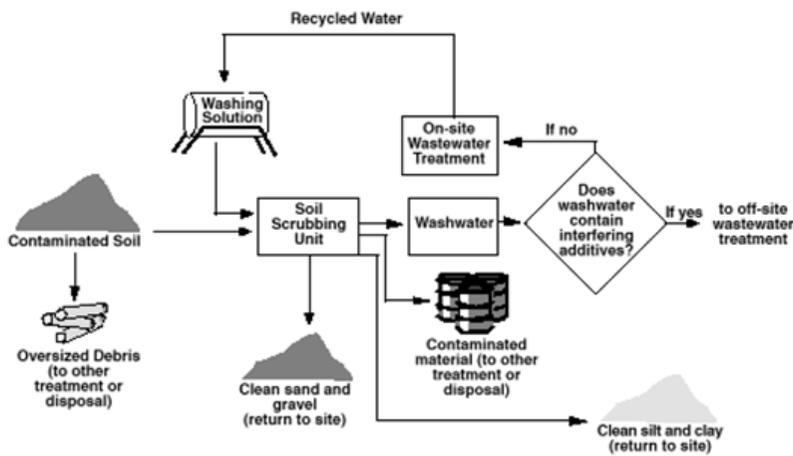


Fig. 2.1 Typical soil washing process (USEPA, 1996d)

Figure 2.1 shows typical soil washing process as starts from excavating, screening soil to separate debris, and soil scrubbing process. In soil scrubbing unit, soil and washing solution is put together and dissolution process is happened. In the past, soil washing only used water as the washing solution. Soil washing theory is based upon the physiochemical processes that occur between the solid particles of soil and the solution in which they are dispersed (Sharma and Reddy, 2004). In general, soil washing is based on the principle that contaminants are likely to adhere to the fine grained soils, which, in turn, are likely to adhere to the coarse grained soils (through adhesion and compaction). Washing with water and possibly additives allows the coarse grained soils to separate from the contaminated fines. Several physiochemical processes such as desorption, complexation, dissolution / solubilization, and oxidation reduction are involved in soil washing (Sharma and Reddy, 2004).

Along with the time, the development of soil washing is continuously increasing by substituting water as washing solution by chemical agent. There are three type of washing solution that usually used in soil washing; surfactant, organic solvent (e.g. HCl, HNO₃, citric acid), and inorganic solvent (chelating agent). In the ex-situ soil washing method, chelating agents and strong acids are used to enhance heavy metal removal (Sun et al. 2001). The type of extractive agent needed for the specific soil washing process depends on the class of contaminant and the soil type. The type of basic aqueous solutions used as extractive agents include caustic lime, slaked lime, or industrial alkali-based washing compounds. On the other hand, an acidic or chelating agent is used to remove organics and heavy metals. Those acidic solutions include sulfuric, hydrochloric, nitric, phosphoric, and carbonic acids. Organic-solvent washing agents are also used to remove hydrophobic organics and PCBs. Oxidizing agents, such as hydrogen peroxide and sodium hypochlorite, can chemically change the contaminants and often facilitate the washing process (USEPA, 1988).

In general, the effectiveness of soil washing can rely on types of soil, types of washing solution, and types of contaminant. In addition, time needed to clean up using this method depends on several factors, such as amount of silt, clay, and debris in the soil, amount of pollution, and size of scrubbing unit (USEPA, 2001). Soil washing is most effective for removing halogenated volatiles, nonhalogenated volatiles, and metals contained in sandy and gravelly soils. However, contaminants can be difficult to be removed and strongly attach to soil, soil which has silt and clay soil in high amount, around 20-30% (USEPA, 1988).

2.1.1. Acid Washing Dissolution Process

There are two typical mechanism in acid washing; (1) Desorption metal via ion exchange, (2) Dissolution metal compounds and/or dissolution soil mineral (Fe-Mn oxides) which may contain metal (Tampouris et al. 2001). The protons in solution at low pH, reacts with the layer silicate and/or surface functional groups (e.g., Al-OH, Fe-OH, and -COOH) of soils, and the desorption rate of metal ions increased (Isoyama and Wada, 2007). Because it has higher affinity than metals, it will replace metal with ion H^+ in soil surface, then metal will dissolve in liquid as an ion state. The dissolution of Fe- and Al-oxides and phyllosilicates occurs when strong acidic fluid is added to the soils, and it replaces the ion exchange process during metal extraction (Kuo et al. 2006).

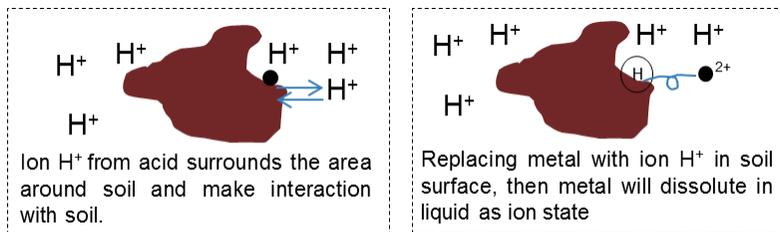


Fig. 2.2 Mechanism of acid washing process

Although hydrochloric acid has great capability for dissolving heavy metal, using it in soil washing has some disadvantage. Soil structure and mineral might be altered by this strong acid solution. This metal leaching induces co-dissolution of soil components causing approximately 50% losses of soil mineral (Tampouris et al. 2001) and organic matters (Ko et al. 2005). It will also affect soil microbiology and fertility (Dermont et al. 2008). In economic view, it becomes an issue because co-dissolution not only increases

the consumption of acid reagent and the complexity of the effluent management, but also the acidity of treated soil is increased. Complexity in effluent management comes from the neutralizing requirement in wastewater treatment. Neutralizing process will create enormous amount of toxic residue (Dermont et al. 2008).

2.1.2. Chelating Agent Washing Dissolution Process

Chelation is a chemical combination complex in which the metal is a part of its ring. Organic ligand is called chelator or chelating agent. The larger number of ring closures to metal atom makes the compound more stable. Chelating agent offers alternative washing solution in soil washing. It can form six-fold coordination with metal and form metal complexes which thermodynamically stronger than soil-metal interaction. This complex is also soluble in water. From a kinetic point of view, the extraction takes place relatively quickly in the first minutes (Barona et al. 2000).

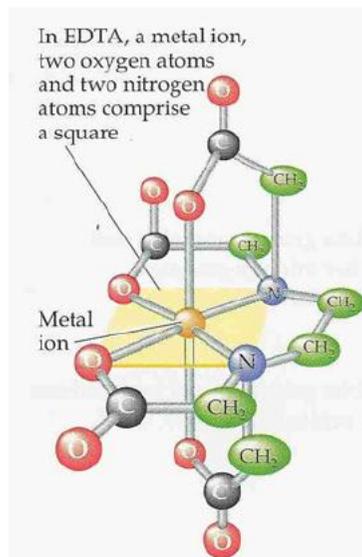


Fig. 2.3 EDTA formation with metal (Tsezos et al. 2016)

Among chelating agent, EDTA is recognized as the most synthetic chelating agent to remove heavy metal (especially Pb, Cd, Cu, and Zn), which have nitrogen atoms and short chain carboxylic groups. It can strong attach cationic metal and broad range of soil types (Dermont et al. 2008). Carboxylic

acid in EDTA formation is also hydrolytically stable at high temperature (USEPA, 1994). Compared to EDTA, EDTA in disodium salt form ($\text{Na}_2\text{-EDTA}$) is more often used as the washing solution because of its more solubility in the water. The sodium salt of EDTA is used as an antidote for metal poisoning, an anticoagulant, and an ingredient in a variety of detergents.

However, EDTA presents some disadvantage points. In the economic point of view, the price of EDTA is very expensive. EDTA also may have probability to pose serious ecological threat if it is not recycled or destroyed in proper way because of its low biodegradable. Furthermore, it has potential for remobilizing heavy metals in the environment (Lim et al. 2005). Even it has strong affinity with cation metals, EDTA is reported ineffective for extracting anionic metal (Dermont et al. 2008).

In the aging effect of contamination, it is started with the adsorption of contaminant into the soil, which contains of film diffusion and the formation of an electrostatic bond. With increased reaction of time, a chemical bond may develop between the ion and surface functional group. Despite the strong retention, the ion may migrate along the surface (surface diffusion) into the interior of the particle, upper pathway in Figure 3. It is also possible that once within the micro pore, addition material (mineral or organic) may coat the particle and occlude the micro pore (bottom pathway). In either case, contaminants become less susceptible to release into the aqueous phase (National academy of sciences, 2003).

2.3. Contaminated Aggregation Soil

Soil in aggregation state is promoted by high ionic strength, which allows particle flocculation (or the bridging of individual precipitates). In this state, soil has low porosity and there are also existences of entrapped pores in the soil. With low porosity, it affects too in low permeability. An individual aggregate might have a 0.35 porosity within it, but the medium as a whole has additional pore space in the form of gaps between aggregates, so that ϕ can be 0.5 or greater (Nimmo, 2014). This condition can affect for attaching contaminant because it will limit contact between washing solution and contaminant. There is also a chance for contaminant to be trapped in those pores. In consequences, removal efficiency will decrease.

Aggregate of particles in soils and sediments can be broken up through physical and chemical perturbations, such as increased fluid shear, a decrease in ionic strength, a change in electrolyte compositions from divalent to monovalent cations, the introduction of a reductant, or a change in pH (Bunn et al., 2002).

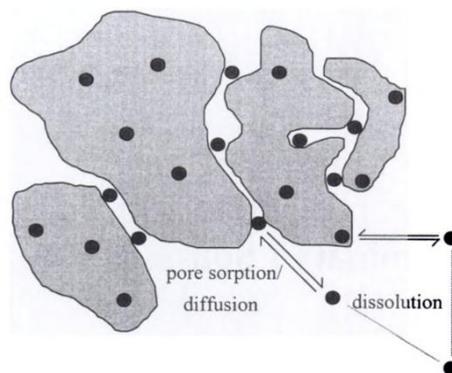


Fig. 2.5 Contaminant in soil aggregation

CHAPTER 3 MATERIAL AND METHOD

3.1 Soil Sample

The soils were collected from an abandoned train maintenance depot site in Yongsan Area, Seoul, South Korea and found contaminated with organic material and heavy metals. However, in this study, target contaminant is limited only to three highest concentrations of heavy metals; copper (Cu), lead (Pb), zinc (Zn). Before test, soil samples were air dried for 3 days. For this study, the soils below 4.75 millimeter (ml) were used, thus rocks and debris were discarded by No. 4 sieve. Physical and chemical properties of the soil samples are listed in Table 3.1.

Table 3.1. Physical and chemical properties of soil sample

<i>Soil properties</i>	<i>Content</i>
<i>pH</i>	<i>7.97</i>
<i>Organic content (%)</i>	<i>8.50</i>
<i>CEC (cmol/kg)</i>	<i>16.29</i>
<i>Bulk density (g/cm³)</i>	<i>0.91</i>
<i>Specific gravity (g/cm³)</i>	<i>2.21</i>
<i>Water content (%)</i>	<i>17.98</i>
<i>Soil Classification</i>	<i>Loamy sand¹</i> <i>Well graded-sand²</i>

¹: USDA; ²: USCS

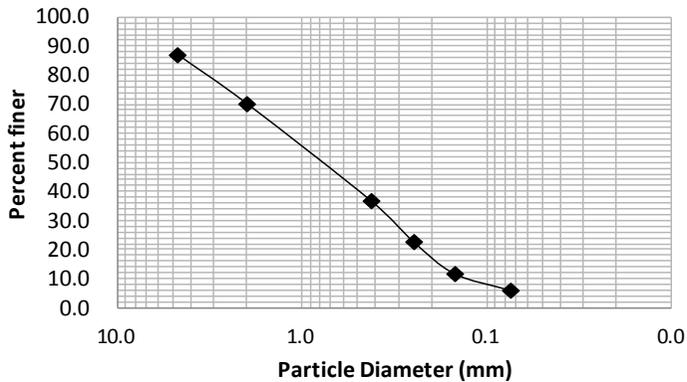


Fig.3.1 Particle size distribution of soil sample

The soil contained not only soil particles itself, but also some industrial wastes and their fragments. Wood chips, bricks, some metal flakes, and other small wastes were found spread evenly in the sample. However, due to their small sizes, it was hard to separate them from the sample. In consequences, the wastes are included in the soil sample.



Fig. 3.2 Soil and wastes inside soil sample

a) Sample collected from the site; b) Several kinds of wastes inside
(From left to right: wood chips, fragile material, bricks, and metal flakes)

Figure 3.3 below shows sequential extraction result of soil sample. Sequential extraction test was conducted in order to find out the fraction percentage of sample. Conceptually, the solid material can be partitioned into specific fractions which can be extracted selectively by using appropriate reagents. The use of sequential extractions furnishes detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization, and transport of trace metals.

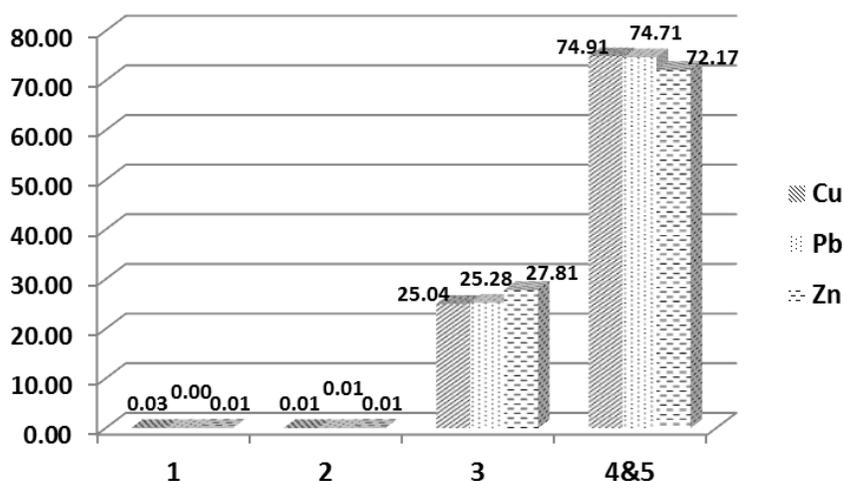


Fig. 3.3 Sequential extraction of soil sample

Fraction 1 is an exchangeable fraction which likely affects sorption and desorption process. Fraction 2 is for significant trace metal concentrations which associated with sediment carbonates. This fraction would be susceptible to changes of pH. In Figure 3.3, it shows that almost the fraction of heavy metals in the sample is in these

fractions. Around 25-27% fraction of heavy metals are in fraction which bound to Iron and Manganese oxides (Fraction 3). Iron and manganese oxides exist as nodules, concretions, cement between particles, or simply as a coating on particle. This fraction is thermodynamically unstable under anoxic condition.

Most of heavy metals particles are on fraction 4 and 5. Fraction 4 is particle which bound to organic matter; fraction 5 is for residual. The sample used in this study is sample come from railroad area, which contains not only heavy metals but also organic matter, like oil. In consequences, heavy metals in fraction 5 has higher portion in the results.

3.2 Chemical Agent

There are two kinds of washing solution used in this study; hydrochloric acid (HCl) and disodium salt of EDTA ($\text{Na}_2\text{-EDTA}$) as chelating agent. Those washing solution were be used separately as single solution and also for sequential method. The results then are compared to each other and the best condition would be applied into the next step. The type of dispersing agent that commonly used is sodium hexametaphosphate (NaPO_3)₆. It usually used for breaking soil aggregation particle in hydrometer test for measuring soil particle. This dispersing agent works in modifying the electric charge on the surface particle and introduce steric barrier that increase stability (Bieleman, 2000). In water treatment, it is usually used to remove a combination of inorganic and organic matter as well as living microscopic organisms. Variation condition in this experiment is shown in Table 3.2 below.

Table 3.2. Variation of washing Solution and dispersing agent concentration

<i>Washing solution</i>	<i>Concentration Variation (M)</i>
<i>Na₂ - EDTA</i>	<i>0.01; 0.01; 0.05; 0.1; 0.2</i>
<i>Hydrochloric Acid (HCl)</i>	<i>0.05; 0.1; 0.2; 0.3; 0.5</i>
<i>Dispersing Agent</i>	<i>Concentration Variation (%)</i>
<i>Sodium Hexametaphosphate</i>	<i>0; 0.5; 1; 1.5; 2</i>

3.3 Lab Apparatus

In this study, 1000 milliliter (mL) volume of heating mantle was used as the soil washing apparatus. It was equipped with two-paddle agitator and stirring speed controller. Temperature can be changed by setting up the machine at the bottom and close the heating mantle with its cap, to make closed system.

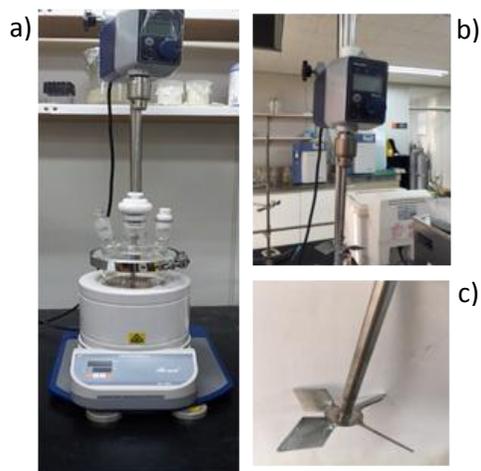


Fig. 3.4 Heating mantle

a) Full equipment of heating mantle; b) Stirring speed controller; c) Two-paddle agitator

3.4 Experimental Concept

A variety of soil washing process has been developed. Most of research focused on enhancing the performance only in chemical aspect, as determine the best solution to be applied in the specific contaminated soil by several kinds of trial and error experiment. In this research, physical and thermal effect is added after determine the best condition in chemical reaction in order to enhance removal efficiency.

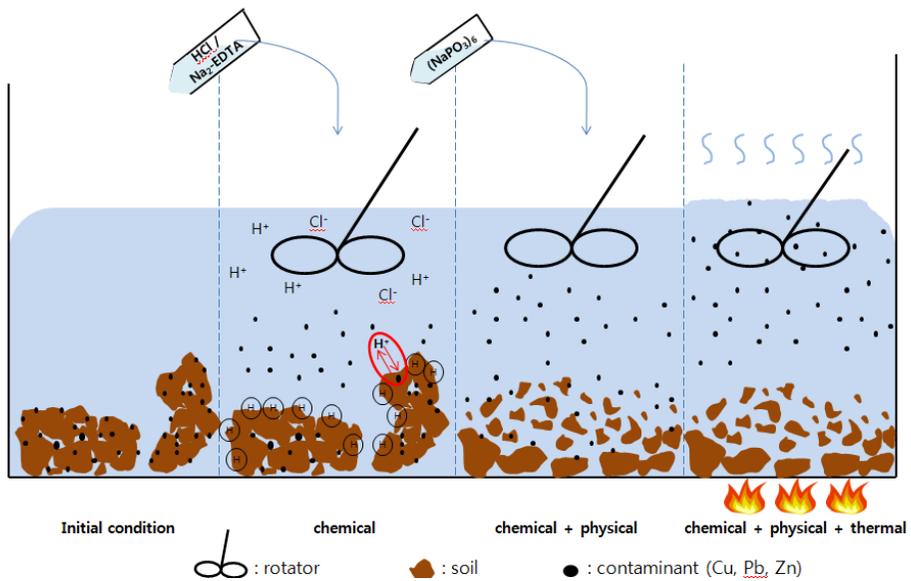


Fig. 3.5 General concept of the experiment

Figure 3.5 shows the general concept of the experiment. The brown things are representative as the soil, and the black ones are representative as contaminant, in this case heavy metal. The first stage is chemical optimization, which has the basic concept to remove contaminant from solid phase to solution phase by dissolving it in washing solution. For example, when HCl is put in the system, ion H⁺ from acid will surround the area around soil and

make interaction with soil. Because this washing solution has higher affinity than heavy metal, it will replace metal from soil surface, then metal will dissolve in liquid as ion state.

The second stage is adding physical effect in chemical reaction before by putting dispersing agent into the system. A dispersing agent prevents flocculation, or the combining of suspended matter into aggregates to accelerate settling out. The main principle of this physical enhancement is how to break contaminant from the aggregation state into the smaller size. It is because soil in aggregation state has low porosity and has existence of entrapped pore. This kind of condition limit contact contaminant from washing solution, in consequences, it will reduce efficiency (Karthileyen et al, 2013). Furthermore, long term contaminated soil also will have susceptible form of heavy metal in interior soil particle. This dispersing agent will break the aggregation form of soil so the chance of contaminant to be isolated will decrease.

The last stage is adding thermal effect after optimization in chemical and physical aspect. When metal is adsorbed in soil surface, exothermic reaction happened. If some thermal is put in this state of condition, it will favor mobilization or molecular movement. In consequences for removal, collision of metal solution will enhance (James, 2006; Madadian et al, 2013). Moreover, it also supplies gibbs free energy for dissolution process (Smith and Martell, 1987; Vallet et al, 2003; Yong Do and Park 2011).

3.5 Lab Experimental Method

Generally the experiment was divided into three main parts; optimization of chemical condition, enhancing chemically soil washing by adding physical effects, and enhancing physico-chemically soil washing by adding thermal effect into the system. To examine the effect of chemical factors, three sets of variation condition, such as (1) washing solution concentration, (2) solid liquid ratio (S/L), and (3) washing time, were conducted in the order. The variation condition is shown in Fig. 4. The best condition in each set is applied into the next step. Best condition was determined based on the effective removal efficiency value. These chemical optimization tests were tested at room temperature.

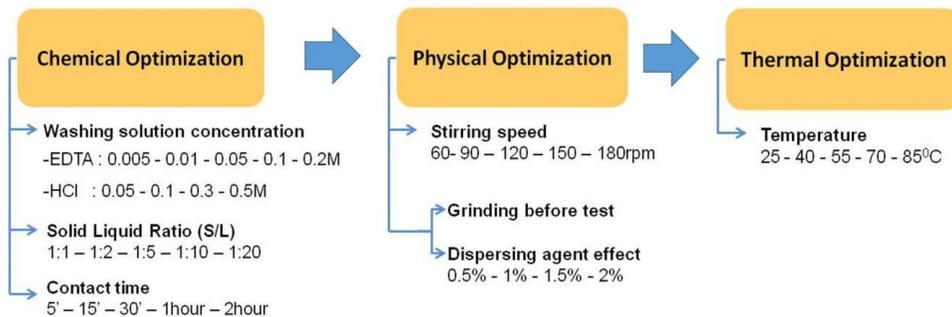


Fig. 3.6 Procedure of lab experiments

Variation of washing solution concentration tests (Table 2) were conducted with the initial condition as 1:5 for S/L and 120 rpm for stirring speed in 30 minutes, for each Na₂-EDTA and HCl. After getting the best condition of single usage of them, it was compared to the sequencing tests; by using Na₂-EDTA then followed by HCl, and also in the reverse order. To

compare with the same condition, the value of S/L and time in sequencing tests were scaled down to half of the single test.

The addition of physical effects were tested by optimization of stirring speed as the component inside the system, and adding component from outside the system, either adding dispersing agent or manually grinding the soil before putting into the system. Lastly, thermal effect would be added by increasing temperature inside heating mantle from 25 °C, 40 °C, 55 °C, 70 °C, until 85 °C.



Fig. 3.7 Manually grinding the soil with mortar

3.5.1 Extraction method

According to ISO 11466, heavy metals from the soil were extracted by Aqua Regia Extraction method, which is mixture of two strong acids; HCl and HNO₃ in the ratio 3:1. It is widely used for determination of the contents of harmful chemical elements in the soil (Taraškevičius et al. 2013). Aqua regia extraction representing total pool of trace metals in soil, showed good correlation between each other for all of the investigated trace metals (Ivezić et al, 2013).

For this experiments, it was conducted by putting 1.5 gram of soil into 12 ml of aqua regia solution (1/3 HNO₃ +2/3 HCl). It was kept for 16 hours in the room temperature for oxidizing organic material). After that, temperature was increased up to 85 °C and set for 2 hours. After insoluble residual settled down, supernatant was transferred to D.I water for diluting. Lastly, diluted solution was filtered by membrane filter and ready to be measured in Atomic Absorption Spectrometer (AAS).



Fig. 3.8 Aqua regia extraction

CHAPTER 4 RESULTS AND ANALYSIS

4.1 Pre-investigation

Pre-investigation was conducted because of the high fluctuation of initial concentration measured. Figure below shows the high range of variation concentration from 25 times measurement of the same sample. It varies from 1069 mg/kg to 2870 mg/kg for Cu, 873 mg/kg to 3300 mg/kg for Pb, and 279-829 mg/kg for Zn. The heterogeneity was presumed to come from the existence of debris of waste inside soil sample and also from metal concentrated in small particle size. However, small size and high quantity of wastes made it hard to separate them from the samples.

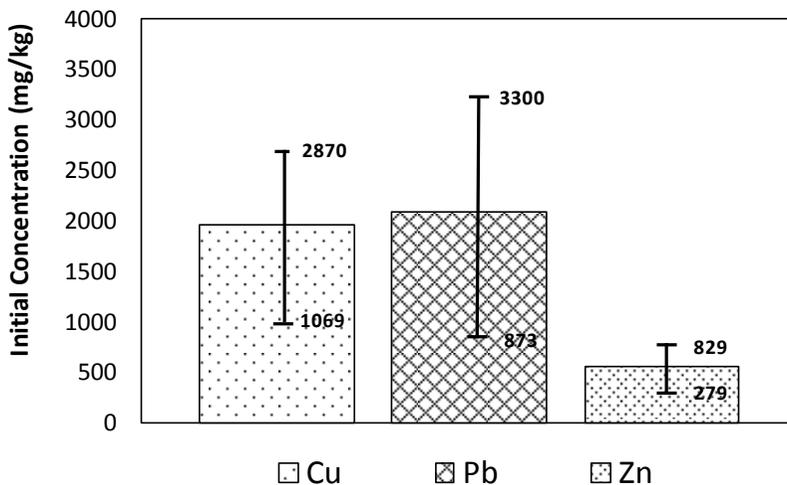


Fig. 4.1 Range fluctuation of initial concentration

In consequences, initial concentration could not be fixed in a constant value so the removal efficiency calculation is not calculated by standard

formula. For more accurate result, the calculation then was approached by mass balance calculation, as shown in the equation (1) below:

$$\%Efficiency = \frac{\text{Contaminant mass in wastewater}}{\text{Contaminant mass in wastewater} + \text{contaminant mass in soil after test}} \quad (1)$$

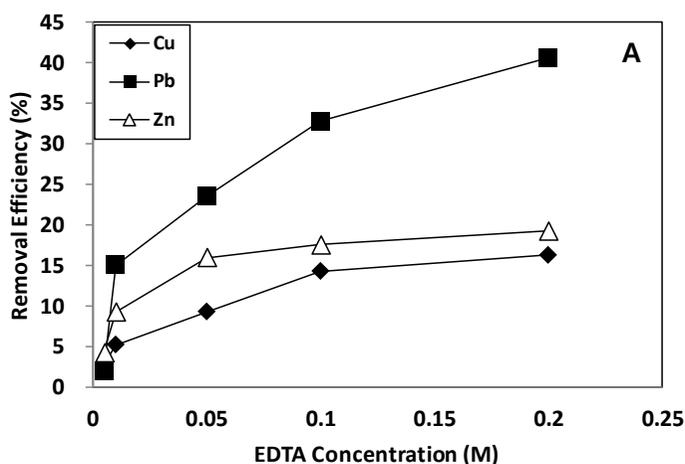
4.2 Chemical Optimization

4.2.1 Washing Solution Concentration

First test was conducted under conditions of: 30 minutes of washing time; 1:10 of solid-liquid ratio; 120 rpm of stirring speed. The results (Fig. 4.2a, 4.2b) show that both washing solution had a tendency to increase in removal efficiency with increasing of washing solution concentration. The order of desorption metal was Cu as the least desorbed metal, followed by Zn, and Pb as the most desorbed metal. Research from Moutsatou et al. (2006) with also has shown that Na₂-EDTA and HCl have excellent performance for Pb and Zn, but intermediate performance for Cu. For copper, the reason was predicted because it has least affinity to be absorbed due to its attribute as the most complex metal and has highest bonding preference with Fe and Al oxides in soil structure. Copper also has high stability constant for organic matter, with the value of organic copper as 10^{11.8} (Hirose et al. 1982, Sun et al. 2001), while the sample also has amount of organic material. So most of Cu was predicted stable attached in organic matter inside the sample and hard to remove them from the sample.

In HCl solution result, removal of Zn and Pb were shown not much different, however, in EDTA case, performance of Pb removal was much greater than Zn. It was because EDTA has higher affinity to make a complex with Pb (Pb²⁺-EDTA) than Zn (Zn²⁺-EDTA). Research conducted by Kim et al. (2013) and Yin et al. (2014) also shown the similar phenomenon like this experiment.

The result of the best condition of Na₂-EDTA (0.2 M) and HCl (0.5 M) then were compared to sequential test. In sequential test, two kinds of tests were done; 0.2 M Na₂-EDTA-followed by 0.5 M HCl, and also in reverse way respectively. Half condition of single washing solution test was applied in sequential test, to make comparison more equal. The removal efficiencies are shown in Fig. 4.2c. It shows that sequential tests worked better than a single used of washing solution. Sequencing Na₂-EDTA-followed by HCl produces higher removal efficiency as 30.0% for Cu, 53.7% for Pb, and 40.7% for Zn. Using Na₂-EDTA in the first stage will help remove organic contaminant layer from the soil which has probability to block the absorption of heavy metals. It is usually applied in removal organic smear layer during rotary root-canal instrumentation (Chen, 2013). In this case, organic contaminant is oil. Then, when this layer had been removed, HCl would more easily detach heavy metals.



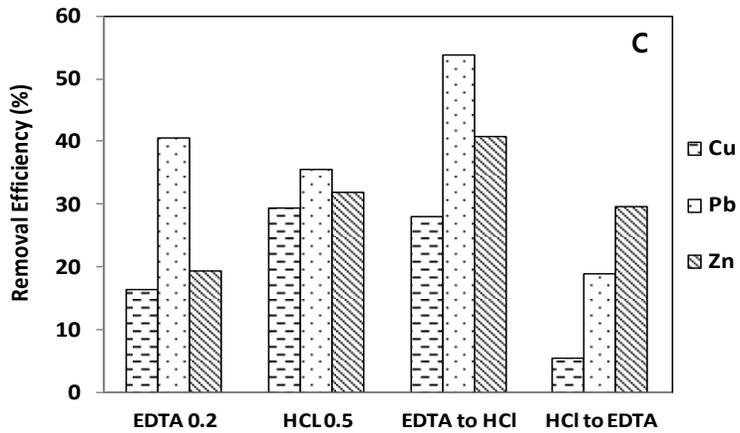
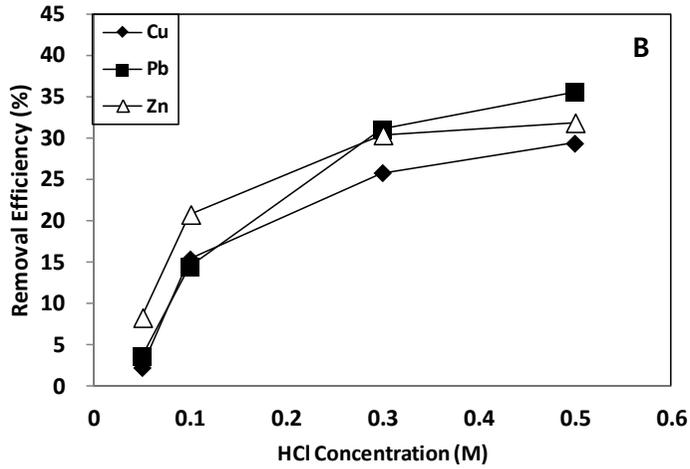


Fig.4.2 Removal efficiency in varied concentration of (A) Only EDTA, (B) Only HCl, (C) Single and sequencing method

However, when using HCl solution followed by Na₂-EDTA, it shows a low performance to remove contaminants from soil. It was thought according to the formation of acid condition in system, which is not compatible for Na₂-EDTA performance. Carboxyl groups of Na₂-EDTA are not dissociated in low

pH so chelating heavy metals below acid condition was interfered (Swayer and Tackett 1962). Moreover, condition of high $\text{Na}_2\text{-EDTA}$ concentration and low pH favors re-adsorption of metal-EDTA to soil solids (Lim et al. 2004). Due the same reason, mixing together washing solution of HCl and $\text{Na}_2\text{-EDTA}$ cannot be conducted.

4.2.2 Solid – Liquid Ratio

Solid-liquid ratio is an important parameter in designing soil washing plant and also shows washing solution capacity to absorb the contaminant target. High S/L means more washing solution used, so conceptually it should shows indicates greater capacity. This test was carried on the same initial condition as test 1 before, for time and stirring and best condition in washing solution (sequential of 0.2 M Na₂-EDTA and 0.5 M HCl).

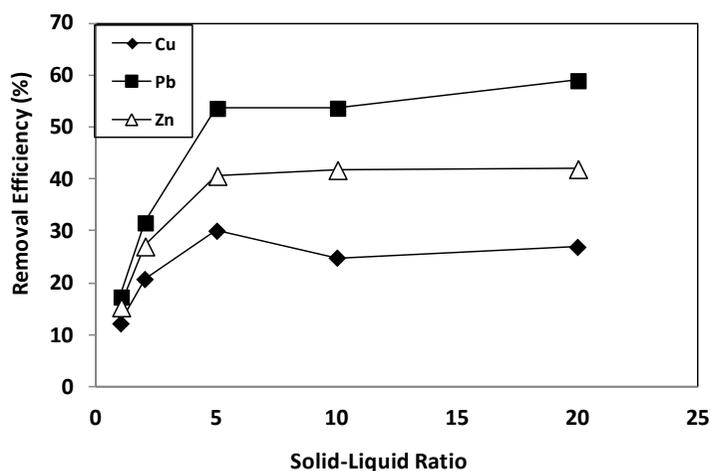


Fig.4.3 Removal efficiency in varied solid-liquid ratio

In Figure 4.3, it can be seen that removal efficiency increased steeply until 1:5. Hence 1:20 shows the highest removal efficiency, 1:5 was chosen as the best condition since the gaps performance of 1:5 and 1:20 only slightly difference. Furthermore, higher S/L will produce more wastewater, which will need a treatment later. In the application, the higher S/L also indicates bigger size of soil washing plant design and more energy due to its huge volume (Peng et al. 2011).

4.2.3 Contact time

Contact time test was conducted with the best condition of washing solution concentration in test 1 and S/L 1:5 as the best condition of S/L in test before. Stirring speed was same with the initial condition, which was 120 rpm. Fig. 4.4 shows that the removal ratio had a relatively quick increased until 30 minutes. However, it would become constant latter in 1 and 2 hours.

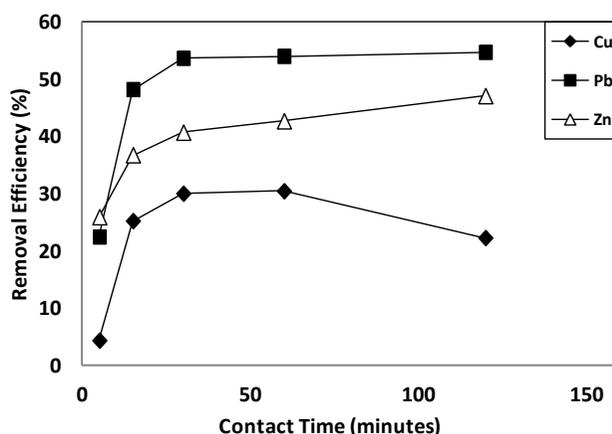


Fig.4.4 Removal efficiency in varied contact time

For Cu removal, mixing soil-solution until 120 minutes had decreased in performance. In HCl mixing process, precipitation of metal-Cl₂ complex was found as the reason of decrement in the removal efficiency. In a long mixing time ion Cl⁻ becomes excessive in the system and makes precipitation of metal-Cl complex, which later, it would re-dissolved again (Moutsatou et al. 2006). In case of Na₂ - EDTA, the metal - Na₂-EDTA solubility became inconstant and less stable in further mixing because of the increment of pH value. Furthermore, it also has possibility for Na exchange with Fe in soil surface. Although in this study Cu removal decreased in performance in 2

hours mixing, further study should be needed for re-check this status before applying in field. According to the results obtained, the best condition was chose as 30 minutes as the equilibrium time in the test.

4.3 Physical Optimization

4.3.1 Rotator Speed

For breaking aggregation soil, changing speed of stirring bladder inside the system was tried first. On Fig.4.5, it shows that interaction of washing solution and contaminant was not good in slow speed, under 90 rpm. When it increased up to 120 rpm, all of heavy metals removal increased significantly. The increasing removal efficiency was presumed to be caused by the collision between soil particles which became stronger in high stirring speed. It would help to make contaminants crusted and get out from the soil easily. On the other hand, stirring speed over 150 rpm causes slurry to move in bulk formation, making low in relative movement. In account of that, the collision was reduced (Peng et al. 2011). Even Zn 150 rpm was found as the best performance for Zn, by considering removal efficiency result of Cu and Pb and also energy usage for making faster speed, 120 rpm was chosen as the best condition for this experiment.

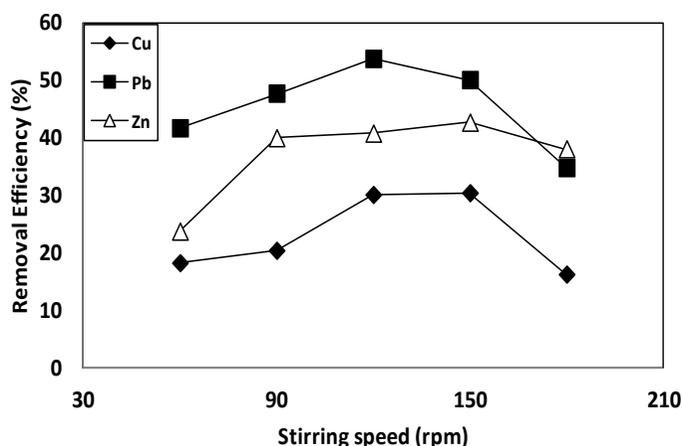


Fig.4.5 Removal efficiency in varied of stirring speed

4.3.2 Comparison of Manual Grinding and Dispersing Agent

After optimizing physical aspect inside the system, the next step was the addition of physical effects outside the system. In this step, comparison of adding dispersing agent into the system and grinding manually the sample before it was put into the system were tested. Those methods have similar purpose; breaking soil aggregation of sample. For grinding test, soil was grinded using mortar manually before putting the soil into the apparatus. On the other hand, in dispersing agent tests, un-grinded soil was used.

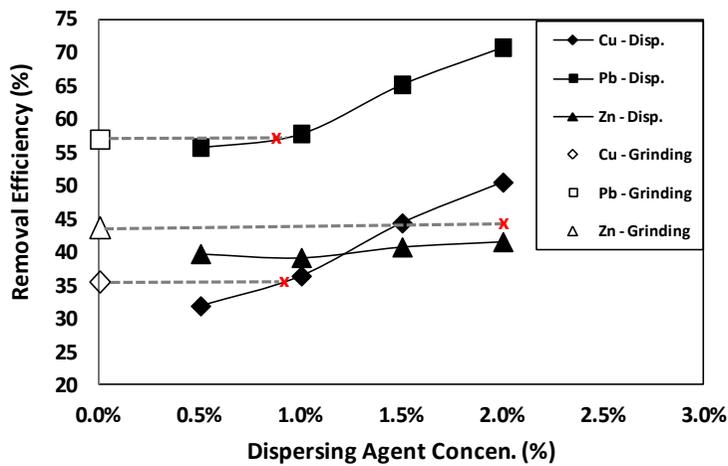


Fig.4.6 Comparison of removal efficiency in varied dispersing agent and manual grinding

Comparing the effectiveness, grinding result test shows similar result with the usage of dispersing agent 1% for Pb and Cu removal, while using dispersing agent above 1% shows a better result. In case of Zn, grinding test

shows slight better performance than using 2% of dispersing agent. Still, using dispersing agent was chosen as better way to enhance soil washing performance because grinding method need energy input for the application. Aggregation is initially promoted by high ionic strength, which allows particle flocculation (National Research Council 2003). In this state, soil has low porosity and it will limit contaminant to be attached (Karthikeyan et al. 2003). By using dispersing agent, soil particle charges could be neutralized and the soil aggregate can be destructed (Bowles 1998). It also affected in breaking entrapped pore in the soil so susceptible contaminant can contact directly with washing solution. The best condition is chosen as using 2% dispersing agent.

4.4 Thermal Optimization

High temperature is known as a factor to increase kinetic energy of ion exchange (Fang 1997). It also enhances the movement of reagent solution in soil washing (Gitipour et al. 2015). Based on this concept, enhancement can be predicted by searching the optimal temperature for metal-solution reaction. In Fig. 4.7, it shows that increasing temperature up to 70 °C could increase performance of soil washing, especially for Zn and Cu. In case of Pb, even not as much as Zn and Cu, removal efficiency also increased. This result is also supported by research of Madadian et al. (2013) that shown increasing in soil washing performance in increasing temperature from 20 °C to 80 °C, because of enhancing collision between washing solution and contaminant by accelerating molecular movement. Increasing temperature can also affect in eroding solid particle in soil for direct desorption of metal.

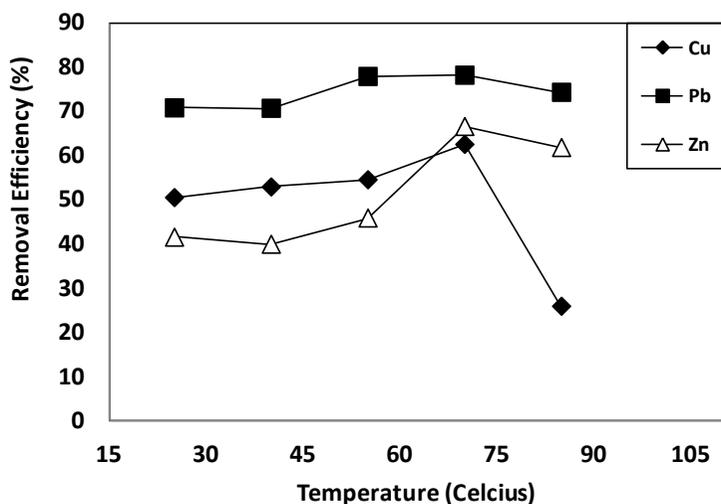


Fig.4.7 Removal efficiency in varied temperature

In contrast, increasing temperature up to 85 °C reduced in the performance, especially for Cu. Research conducted by Kumpiene et al. (2016) stated that thermal treatment could lead to formation of Cu oxides with low solubility leading to the decreased leaching of this element. At high temperature, copper in CuO / Cu₂O would form (Cu₃(PO₄)₂). This phenomenon might also present in thermally treated soils. Another prediction also came from stabilized heavy metal due to solidification in thermal process (Bayuseno et al. 2009; Jing et al. 2010, Singer and Berggaut 1995). Similar in contact time test for decreasing in Cu removal, this phenomenon should be rechecked before applying in the field.

4.5 Combination Effect and Application

The result below (Fig. 4.8) shows the escalation performance of soil washing, starts from optimization in chemical aspect, adding physical aspect in chemically optimized soil washing, and combination physical and thermal effect into chemically soil washing. Those three aspects; chemical, physical and thermal, if put together into one system was proved to enhanced removal efficiency in this experiments. Compared to chemical soil washing alone, this combination effect increased performance up to 50% for all heavy metals. Even the addition of physical effect was found not bring the increment of removal efficiency, but after adding thermal, removal efficiency significantly increased to 66.51%.

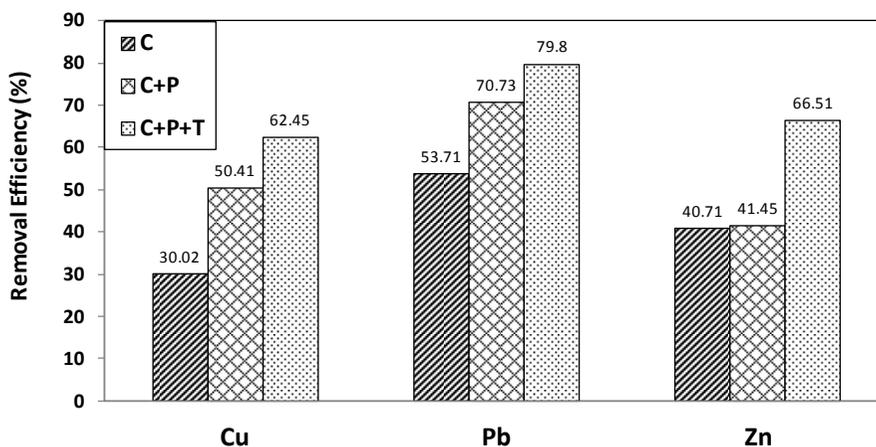


Fig. 4.8 Effect of the addition of physical and thermal in efficiency

This result, then, was tried to be applied in the site by comparing with Korea's soil Regulation Standard from Ministry of Environmental (MoE) first. For the calculation, it was using the high value of initial concentration

for each heavy metal. In this standard, Korea's Government divided the area into three zones, which each zone has different limitation of heavy metal concentration. Zone 1 is for fields, paddies, residential area, school sites, parks, and children playground. Zone 2 is allocated for forests, building non-residential, rivers, recreational sites, and warehouses. Thus, zone 3 is for factory sites, gas station sites, roads, parking loads, railway, and military facilities.

Table 4.1. Korea's standard soil regulation

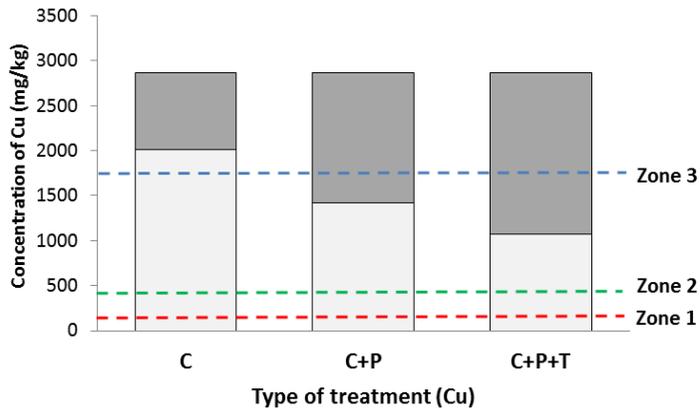
<i>Heavy Metals</i>	<i>Limit Concentration (mg/kg)</i>		
	<i>Zone 1</i>	<i>Zone 2</i>	<i>Zone 3</i>
<i>Copper (Cu)</i>	150	500	2000
<i>Lead (Pb)</i>	200	400	700
<i>Zinc (Zn)</i>	300	600	2000

The application of results on Korea's soil regulation standard is shown in Figure 4.9. Treatment with only chemical aspect cannot pass standard regulation for any area, for Cu and Pb. On the other hand, only chemical treatment will make pass this area into zone 2. By putting the physical enhancement in chemically soil washing, Cu can pass the regulation to zone 3. However, putting thermal into the system brings no more effect to pass zone above 3.

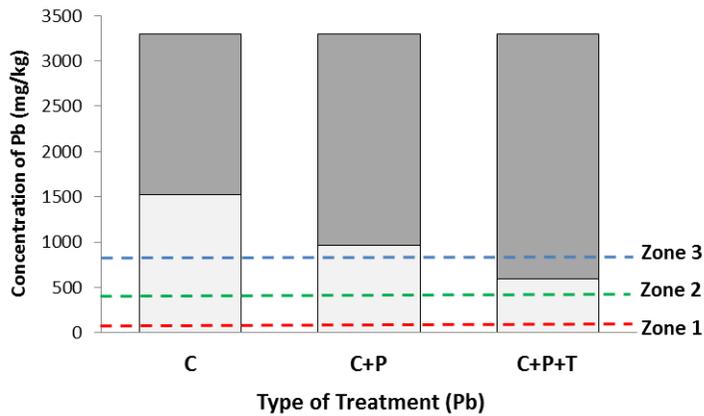
Lead (Pb) is the highest removal concentration in this research, yet the highest concentration in the sample. By using only chemical and also physically soil washing, it seems not bring any effect for passing pass to minimum limit concentration at any zone. The only way to pass the regulation is using chemical, physical, and thermal together to pass zone 3.

Without any treatment, zinc condition is available to be applied in zone 3. However, adding physical treatment will not bring any changing in

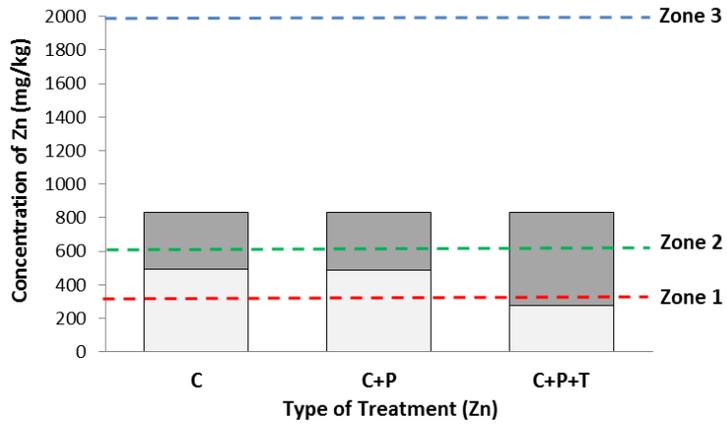
removal efficiency, so it will stay in zone 3. Furthermore, adding thermal effect makes this sample safe to be used for zone 1. This representation will help to choose what kind of treatment and which zone is the target after treatment. It can be fit also with the effectiveness in cost and also energy.



(a)



(b)



(c)

Fig. 4.9 Application results in Korea's soil regulation standard for (a) Copper (Cu), (b) Lead (Pb), and (c) Zinc

CHAPTER 5 CONCLUSIONS

Combining three main effects (chemical, physical, thermal) in soil washing was proved could enhance the performance of soil washing, compared with general chemically soil washing. Optimization in chemical aspect illustrated the general idea how chemical factors effect soil washing process and set as the best condition for applying combination treatment. Optimal condition in chemical aspect was reached in 1:5 solid-liquid ratio and contact time for 30 minutes, which using sequence using Na₂-EDTA followed by HCl in the second step. Breaking aggregation soil to enhance performance had been conducted by changing speed of stirring bladder and putting dispersing agent into the system. Lastly, increasing temperature up to 70°C more enhanced performance of soil washing in this experiment.

In the end, these combination effect enhanced removal efficiency from 30.02% to 62.45% for Cu, 53.71% to 79.8% for Pb, and 40.71% to 66.51% for Zn. However, increasing temperature and dispersing agent is predicted to cost more than general chemically soil washing. For the application, it is better to consider target minimal removal and effectiveness in cost and energy. Comparison of cost and energy is surely important to be taken into consideration, but it is not included in this scope of study.

Some additional studies may be recommended to supplement this research:

- (1) Re-checking some decrement in removal efficiency tests.

In this study, the decrement of removal efficiency was found in some variable tests. Re-checking may be needed because those variables are important to be set in the real site.

(2) Measuring the concentration by leaching method.

In this study, concentration was measured by AAS (Atomic Absorption Spectroscopy). Measuring by leaching tests may produce different result and it could be compared with the results in this study.

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초 록

구리, 납, 아연으로 동시에 오염된 철도부지 오염토양에 대한 토양세척연구가 수행되었다. 각 중금속의 오염농도는 구리의 경우 1069~2870 mg/kg, 납의 경우 873~3300 mg/kg, 아연의 경우 279~829 mg/kg 의 범위로 나타났다. 중금속 농도가 비교적 높게 나타났기 때문에, 성공적인 정화를 위해서는 토양세척 조건의 최적화 및 세척 효율 향상이 필요하다. 따라서 본 연구에서는 화학 세척의 최적 조건을 도출하고, 또한 물리적, 열적 방법을 추가적으로 도입하여 화학세척의 효율을 극대화함으로써 전체적인 정화 효율을 증진시켰다. 화학 세척 실험 결과, 0.2M Na₂-EDTA 로 세척한 뒤 0.5M HCl 로 순차적으로 세척하였을 때, 1:5 g/ml 의 고액비에서, 30 분 동안 교반하였을 때, 각각 최적의 효율이 나타났다. 물리적 방법을 통한 세척 효율 증진 실험에서는 120rpm 의 교반속도 및 2%의 분산제를 넣었을 때, 효과적으로 세척 효율을 증진시킨 것을 확인할 수 있었다. 열적 방법을 통한 세척 효율 증진 실험에서는 상온에서 70°C까지 온도가 증가함에 따라 효율이 증진되는 것을 확인할 수 있었는데, 이는 분자 운동의 촉진에 따라 오염물질과 세척용액 간의 반응이 활성화된 것에 기인한 것으로 보인다. 그러나 70°C 이상에서는 효율이 크게 증진되지 않았으며, 구리의 경우 오히려 효율이 감소하는 것으로 나타났다. 본 연구에서 물리적, 열적 효과를 추가함으로써 나타난 세척효율을 기존의 화학세척의 효율과 비교하였을 때, 구리의 경우 30.0%에서 62.5%로, 납의 경우 53.7%에서 79.8%로, 아연의 경우 40.7%에서 66.5%로 각각 증가한 것으로 나타났다.

주요어: 토양세척, 철도부지 오염, 중금속, 물리적 효과, 화학적 효과,
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