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염화철이온을 함유한 시트르산 용액에
의한 광미 중 중금속의 제거

**Removal of heavy Metals from Tailings in Citric Acid Solution
with Ferric chloride**

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Removal of heavy Metals from Tailings in Citric Acid Solution with Ferric Chloride

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Abstract

The release of heavy metals and other pollutants in soil became one of the most important environmental problems. A number of studies and assessments about heavily-contaminated sites indicated the possible health impacts of contaminated soil with high level of metals. To remove such kinds of pollutants, in fact, soil washing plays a role as one of the most permanent treatment alternatives to remove heavy metals from soil contamination. The studied metals in this work included six elements: Fe, As, Mn, Zn, Cu, and Pb from tailings, which have been known as a cause of soil contamination near abandoned mine sites. Furthermore, the sample observed by X-ray Diffraction (XRD) showed the high levels of quartz and metal sulfides components, which made it difficult to remove pollutants by using chemical reagents independently. Thus, the combination of citrate and ferric ion were selected to remove heavy metals from these stable forms.

Firstly, the chemical forms of six metals in contaminated soil were investigated by Tessier's sequential extraction procedures. In that, the heavy metals include five fractions corresponding with five steps in procedures: "exchangeable", "bound to carbonate", "bound to Mn-Fe oxides", "bound to organic matter and sulfide minerals", and "residue". However, the result comparisons between 1.0 g sample suggested by Tessier's and 0.2 g sample in present study showed the differences in distributions. The highest portion of metal species was found in the "residual fraction" with 1.0 g sample and in the "bound to organic matter and sulfide minerals fraction" with 0.2 g sample, respectively. It illustrated that to obtain the exact information of metal distribution from sources with high metal level, the use of less sample should be chosen.

Secondly, the leaching efficiencies of heavy metals were also investigated by the combination of citrate and ferric ion. An investigation of parametric influences on metal extraction exhibited the remarkable increase the leaching efficiencies of heavy metals except As with increasing initial ferric ion concentration, agitation speed, and temperature, but decreasing pulp density and pH solution. It was found that 100 % of total Fe, Mn, Zn, Cu, and Pb concentration were extracted in solution under the conditions of 3.0 M Fe^{3+} , 1.0 M citric acid at 50 °C of temperature, agitation speed 400 rpm, and after 3 h leaching time. The result also showed that the leaching efficiencies of heavy metals except As were enhanced with the presence of citric acid in ferric chloride solution compared to the solution without citric acid. The reducing of oxidation-reduction potential (ORP) can be considered as a main disturbing factor on As dissolution.

KEYWORDS: tailings, citric acid, ferric chloride, sequential extraction, heavy metals, arsenic.

초록

중금속 등의 오염원이 토양에 유출되는 것은 주요 오염 문제의 하나이다. 고농도 중금속 오염토양의 잠재적인 보건상 위험에 관한 연구가 다수 진행되어 왔고, 처리 방법의 하나로서 영구적인 제거방법인 토양세척이 토양오염정화 분야에서 주요한 역할을 하고 있다. 본 연구에서는 폐광산 주변 토양 오염의 주요 원인 금속 6종 - 철, 비소, 망간, 아연, 구리 및 납 -에 대해 제거 연구를 진행하였다. XRD 분석결과 석영 및 황화물이 관찰되었으며, 이는 단순한 침출액을 선정하여 진행하는 것 만으로 중금속 제거가 어렵다는 것을 나타낸다. 따라서 본 연구에서는 시트르산과 3가 철이온을 동시에 사용하여 안정적인 형태의 중금속을 제거하고자 하였다.

첫째, 오염토양 중 여섯 금속의 화학적 형태를 Tessier의 연속추출공정에 의해 조사하였다. 이 공정은 중금속을 이온교환형, 탄산염결합형, 산화물결합형, 유기물 및 황화물 결합형, 그리고 잔사의 형태로 분류하는 방식이다. 기존 공정에서는 1 g의 시료를 이용하여 분석을 진행하나 본 연구에서는 0.2 g의 시료를 사용하고 분석을 진행하였다. 1 g의 시료를 사용하였을 때는 잔사형태에서 가장 많은 중금속이 검출되었으나 0.2 g의 시료를 사용하였을 때는 유기물 및 황화물 결합형에서 가장 많이 검출되었으며, 이는 기존 연속추출법에서 사용되는 시료보다 고농도의 중금속을 함유한 시료를 분석하였기 때문으로 생각되었다.

둘째로, 시트르산과 철이온을 동시에 함유한 침출액을 이용하여 중금속 제거 실험을 실시하였다. 침출요소 중 초기 3가 철이온의 농도, 교반속도, 반응온도를 증가시키기에 따라 비소를 제외한 중금속의 침출농도가 증가하였으나 반대로 광액농도와 pH가 증가함에 따라 침출농도는 감소하였다. 철, 망간, 아연, 구리, 그리고 납은 3가철 이온농도 3.0 M, 시트르산 농도 1.0 M, 반응온도 50 °C, 교반속도 400 rpm, 그리고 3시간의 침출시간 후 100%의 침출율을 나타내었다. 이 결과는 3가철 이온과 시트르산의 동시 이용에 의해 중금속의 침출율이 개선된 것을 나타낸다. 비소의 침출율이 낮게 나타난 것은 시트르산 첨가에 의해 용액의 산화환원전위가 다소 낮아진 것이 원인으로 분석되었다.

키워드: 광미, 시트르산, 염화철, 연속추출, 중금속, 비소

Chapter 1 Introduction

1.1. Research background

Polluted environment has existed in the world for centuries but only started to become one of the greatest environmental problems after the industrial revolution in the 19th century. Since the rapidly expanding human activities, air, water and soil are being accelerated polluted alike. Afterward, soil becomes “universal sink”, which has to bear the greatest burden of environmental pollution. According to Verruijt (2001), soil is a thin layer of complex mixtures of organic and inorganic materials, which are seemed as filters of toxic chemicals and adsorb heavy metals. However, when the pollutants exceed the toxic capacity of soil, it could release the heavy metals into groundwater and be available of plant uptake. Because of the increasing man-made products or the wastes from treatment plants, we are losing this important natural resource and it becomes soil pollution. Hence, soil pollution is defined as the excess of persistent toxic compounds in soil, disease causing agents, radioactive materials, chemical compounds, or salts, which cause adverse effects on the growth of plant, animal and human health (Okrent, 1999).

Nowadays soil pollution is getting significant public attention since the rapidly expanding industrial activities such as mining, smelting, battery production/recycling, intense urbanization and other human activities. These activities accumulate the heavy metals and metalloids through the emissions, which become the major environmental problem throughout the world and increase the global concern. According to the supervision of US EPA (Environmental Protection Agency), in the US over the last decades, almost half a million sites have been reported with potential contamination. Furthermore, in the report of European Commission, a huge amount with 3-5 million potentially contaminated sites and 500,000 sites known as contaminated are situated in Europe (Vanheusden, 2009). It has been known that, mining wastes, including mine tailings, waste

rock and slag are generated from mining operations such as mineral excavation, ore transportation, smelting and refining. These became one of the main sources of environmental contamination until now (Roussel et al., 2000). Mine tailings have released a huge amount of heavy metals such as arsenic-bearing tailings, cadmium, copper, lead, chromium, and mercury, etc. Furthermore, mining activities are the major anthropogenic source of heavy metal pollution and could produce very large amounts of wastes (Laghlimi et al., 2015). According to Kim and his coworkers, there are about 1,500 closed metal mines in South Korea and almost of them have been left without any management (Kim et al., 2001). Lim and his coworkers showed that one of the abandoned metal mine in Korea contained very high concentration of heavy metals with As: 67,336 mg/kg; Fe: 137,180 mg/kg; Cu: 764 mg/kg; Pb: 3,572 mg/kg; and Zn: 12,420 mg/kg (Lim et al., 2009; Jang et al., 2005). Therefore, such kind of contaminated cause was paid much attention due to their significant threats. In order to investigate these potential sources of contaminated soil, samples from Korea mine tailings were collected to examine heavy metals removal efficiencies under the laboratory scale.

In General, heavy metals in soil are not subjected to decompose by biogeochemical processes and persist in the environment for a long time. Otherwise, under several physical-chemical processes, these heavy metals tend to accumulate and remain almost indefinitely on the environment (Akoto et al., 2008; Haribhau, 2012). The accumulated heavy metals enter into the food chain via their uptakes to the food-crops and therefore, pose several threats to human health as a result of excessive accumulation of these metals. Health risks may also be expressed through the dermal or ingestion exposure. Therefore, risk assessments were carried out by several researchers which became an effective tool not only for warning, but also for managing the contaminated sites in cost-effective manner (Zhao & Kaluarachchi, 2002). In fact, the treatment operations are still limited in both wealthy and developing countries due to the cost aspect, insufficient advantages, principles of machine operation as well as the inadequate awareness about health risk problems

(Burlakovs, 2015). Therefore, the treatment method must be chosen carefully and well addressed before applying in commercial scale and it depends on many different aspects.

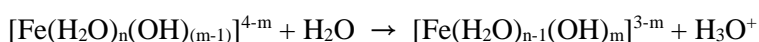
In order to treat and prevent such kinds of heavy metals in contaminated soil sites, a number of remediation processes including chemical, physical, or biological technologies have been applied and developed. Among them, phytoremediation, solidification/stabilization, physical separation (e.g. hydrocyclone, gravity separation) and soil washing are frequently listed among the best available technologies (GWRTAC, 1997). It has been known that gravity separation followed by chemical treatment has been favored in terms of heavy metal polluted source. However, the tailings which are produced as very fine particle size are very difficult to use gravity separation method. Soil washing, on the other hand, in terms of chemical technique, which is also called chemical extraction, uses chemical reagents (chelating agents, salts, acids/bases, etc.) to dissolve metal contaminants into solution. In this solution, metals could be converted to more soluble forms or enhanced the solubility of metal compounds in soil and it is also suitable for the fine contaminated soil particles remediation. It has been known that some strong acids (HCl, HNO₃, H₂SO₄, etc.) and chelating agents (EDTA, tartaric acid, citric acid, etc.) are commonly investigated to extract metals from soils (Stylianou et al., 2007; Yan et al., 2014; Abumaizar & Khan, 1996). Even though strong acids could separate available metals from soil permanently within the short time, they still cause problem when destroying the crystalline soil structures and its properties after treatment. Otherwise, chelating agents have been suggested as alternatives and promising approaches and EDTA was seemed to be the most efficient one for stable complexes and strong chelating ability for various metals (Wuana et al., 2010). Unfortunately, EDTA presents several disadvantages such as expensive reagent, low biodegradable degree and potential for mobilizing (Lim et al., 2005). On the other hand, citric acid is well known for not only the environmentally-friendly product which could be rapidly biodegraded in soil environment, but also cheaper low-molecular-weight acid than others (Astuti et al., 2016). With the use of citric acid, we do not have to concern

about citrate-metal complexes remain in soil after treatment. Therefore, among several available chelating agents, citric acid was introduced in this study to investigate the leaching behavior of metals from soil. However, different researchers illustrated different behaviors of citric acid on metal removal from contaminated soil. Some studies suggested that citric acid could remove effectively heavy metals in soil: 86.5 %, 88.9 %, and 83.3 % for Cu, Zn and Pb (Park et al., 2013). Notwithstanding, other researchers reported that leaching efficiency of citric acid was low (Wuana et al., 2010).

Basically, heavy metals in tailings could be existed in various forms, and these form species may have impact on evaluating the influence on the mobility and bio-availability. According to Tessier et al., (1979), there are five fractions that heavy metals in soil or sediment could be existed: exchangeable, bound to carbonate, bound to Mn-Fe oxides, bound to organic matter/sulfide minerals, and residual fraction. Each fraction could be extracted selectively by using appropriate reagents and about to be affected by environmental conditions. If heavy metals exist in a form that is exchangeable, bound to carbonate or bound to Mn-Fe oxides with weak bonding strength, they can be easily mobilized into the ecosystem. Contrarily, if metals exist in forms of sulfide minerals, organic ligands or held within a crystal lattice which are very difficult to separate soil-metals. A number of studies have reported about leaching ability of citric acid on metal removal showed that citric acid is just able to remove the exchangeable, bound to carbonate and bound to Mn-Fe oxides fraction. However, there is no effect with bound to organic matter/sulfide mineral fraction if using only citric acid solution (Wuana et al., 2010; Park et al., 2013). Moreover, metals in mine tailings usually exist in sulfide minerals forms such as pyrite (FeS_2), arsenopyrite (FeAsS), chalcopyrite (CuFeS_2) (Lim et al., 2009). Therefore, it is needed to enhance the removal efficiency of sulfide mineral and residual metal compounds, which are the main components in mine tailings. It has been well recognized that ferric ion such as ferric chloride (FeCl_3), ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) could play a role as an important oxidative leaching agent. Several investigators have been

studying the leaching efficiency of sulfide metals using ferric chloride and ferric sulfate with excellent results (Al-Harashseh & Kingman, 2008; Santo et al., 2010; Yoo et al., 2016). On the other hand, ferric chloride demonstrates several advantages over ferric sulfate when metal-chloride complexation was reported could enhance the metal extraction (Dutrizac & Macdonald, 1978). Nevertheless, it has several advantages to be widely applied:

- (i) Ferric ion (Fe^{3+}) has a low pK_a value, which could generate hydrogen ion during association with water molecular follow the free energetics of the reactions:



With the produced hydrogen ions from ferric (oxy) hydroxides, pH of solution could be reduced, the metal extraction from soil could be enhanced.

- (ii) FeCl_3 could remove the metal contaminants in soil with high efficiency, cost effectiveness, and has low environmental impact.
- (iii) Furthermore, Fe^{3+} could be re-generated because after producing Fe^{2+} from Fe^{3+} in leaching processes, it can be oxidized electrically or biologically to Fe^{3+} (Lee et al., 2015).

These demonstrations suggested that ferric chloride could play an important role to improve the metal extraction from soil, together with citric acid combination.

1.2. Research objectives

In this present article, we study on removal of heavy metals from the tailings by using citric acid and ferric application with an aim at improving the performance of citrate for extraction of heavy metals:

- To examine and develop the method of chemical forms through the metal distributions of heavy metals in soil using the sequential extraction procedure.

- To investigate the efficiency of soil washing with citric acid and potential application of ferric chloride improvement in laboratory scale with the effects of time, agitation speed, ferric concentration, the effect of with and without citric acid in ferric solution, pH solution, temperature and pulp density on the leaching behavior of metals.
- To assess the Arsenic contamination in soil and potential for removal.

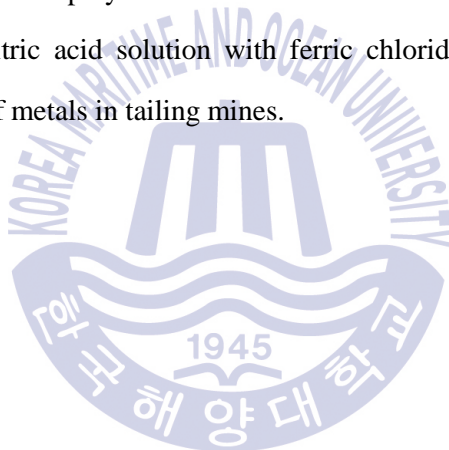
1.3. Research scopes

1.3.1. Tessier's sequential extraction

Mine tailings from abandoned mine was known with very high content of heavy metals. However, the accurate measurements of total metal concentration are just suitable for the potential risk of pollution assessment. In fact, changes in environmental conditions could lead the mobilization of metals from the solid phase to the liquid phase and called weathering fractions. Therefore, the most appropriate soil remediation methods of metals including Fe, As, Mn, Zn, Cu and Pb needs an effective tool to evaluate the characteristic and nature of soil. On the other hand, it is well recognized that the behavior of these pollutants strongly depend on the site characteristic, types of pollutants, specific chemical forms, concentration and the use of the leaching medium. To obtain the speciation of metals in soil, widely used methods for evaluation of heavy metals availability in soil are available. In this study, the sequential extraction method followed Tessier's procedures was chosen. There are five main fractions of metals could be existed: exchangeable, bound to carbonate, bound to Mn-Fe oxides (reducible fraction), bound to organic matter/sulfide minerals and residual fraction.

1.3.2. Leaching experiment

The work about leaching of metal sulfide minerals using chloride media is interesting subject and has been applied by several researchers. Ferric chloride which has several advantages as above description could play a role as the oxidant in leaching systems. In which, under the leaching conditions, elemental sulfur could be liberated during the oxidation process and transfer from solid phase to liquid phase in solution. Citric acid is well known as an alternative extractant not only due to the superior complex formation between citrate and heavy metals in soil but also cheaper reagent than other organic acids. Citric acid then combines with liberated metals in solution to make the complex formation. Finally, soil would be cleaned up by filtration from solution. The basic study for extraction of heavy metals using citric acid solution with ferric chloride has been carried out to investigate the behavior of metals in tailing mines.



Chapter 2 Literature review

2.1. Contaminated soil with heavy metals

Together with large areas of developed countries over centuries, industrial productions, mining and military activities as well as agriculture have produced and accumulated heavy metals day by day. According to Ross (1994), there are five main groups of the anthropogenic sources of metal contamination: (1) metalliferous mining and smelting, (2) industry, (3) atmospheric deposition, (4) agriculture, and (5) waste disposal. Table 2.1 shortly summarized and showed the different sources of various heavy metals (Lone et al., 2008).

Table 2.1 Different sources of heavy metals for contaminated soil

Heavy metals	Sources
As	Semiconductors, petroleum refining, wood preservatives, animal feed additives, coal power plants, herbicides, volcanoes, mining and smelting.
Cu	Electroplating industry, smelting and refining, mining, biosolids.
Cd	Geogenic Sources, anthropogenic activities, metal smelting and refining, fossil fuel burning, application of phosphate fertilizers, sewage sludge.
Cr	Electroplating industry, sludge, solid waste, tanneries.
Pb	Mining and smelting of metalliferous ores, burning of leaded gasoline, municipal sewage, industrial wastes enriched in Pb, paints.
Hg	Volcano eruptions, forest fire, emissions from industries producing caustic soda, coal, peat and wood burning.
Se	Coal mining, oil refining, combustion of fossil fuels, glass

	manufacturing industry, chemical synthesis (e.g., varnish, pigment formulation).
Ni	Volcanic eruptions, land fill, forest fire, bubble bursting and gas exchange in ocean, weathering of soils and geological materials.
Zn	Electroplating industry, smelting and refining, mining, biosolids.

As can be seen in the table above, one of the most significant sources released heavy metals including heavy industries, e.g. mining industry and metallurgy. Metals released by exploiting activities, surrounding landscape, emissions of metallurgical dust containing high level of sulfide lead, arsenic, zinc, copper ores, etc. The quantity and composition of metal pollution are different with different sources, the mining sites and raw materials. It also depends on the weather conditions however, the runoff from the abandoned mines could be extremely acidic due to the chemical and biological oxidation processes by weathering, and the pH can reach values as low as 2 (Hafenburg & Kothe, 2007). Remediation technologies could be classified according to *in-situ* and *ex-situ*. An *in-situ* is a technology that deals with the presented contaminants in soil or groundwater by applying the on-site treatment processes without removing the bulk soil. In this case, the unexcavated soil or groundwater remains undisturbedly after the clean-up processes. *Ex-situ* approaches are remediation options where the contaminated soil and/or groundwater is removed from original location (excavated site) and performed on-site or off-site.

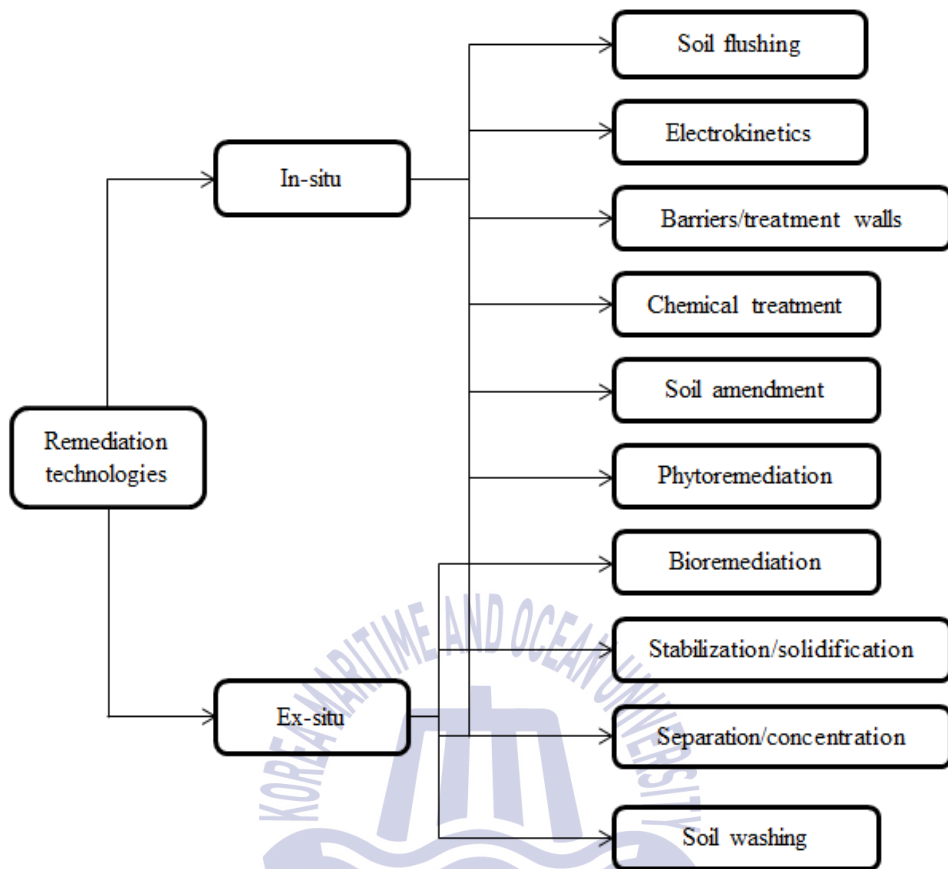


Fig. 2.1 Classification of remediation technologies for contaminated soil.

Among several methods, this study would like to give some reviews of the technologies which are frequently listed among the best available technologies.

2.2. Contaminated soil remediation processes

2.2.1. Phytoremediation

Phytoremediation is based on natural method, alternative or complimentary technology. It is an *in-situ* remediation technology and can be understood as the utilization of plant abilities to remove the pollutants from the environment and their associated microorganisms in order to cleanup, degrade or isolate toxic substances. Due to the extent of contaminated areas and their ecologically friendly method, it has been recognized as a significant scientific and commercial attention (Lone et al., 2008; Chehregani et al., 2009; Mahar et al., 2016). Phytoremediation is a term that has been used for a long time to reduce the concentration, mobility, or toxicity of contaminants in soil, groundwater, or other contaminated media with the use of plants (USEPA, 2000). Phytoremediation treatment method is divided into several forms such as: phyto-extraction (phyto-accumulation), rhizosphere biodegradation, phyto-stabilization, phyto-volatilization, phyto-degradation, etc. However, the most common technologies are phytoextraction and phytostabilization.

Phytoextraction also called phytoaccumulation or phytoabsorbtion; this is the biological method in which the heavy metals in soil could be transferred to the specific species of plants by plant roots under the translocation and uptake processes (USEPA, 2000). Once adsorbed, the heavy metals or its by-products can be stored in the plant biomass. Phytoextraction is not only seemed as the best approach to remove and isolate the contaminants after treatment without destroying the soil structure but also the most suitable for the remediation of low metal concentration and superficially diffusely polluted areas (Ghosh & Singh, 2005). However, the limitations of hyper-accumulator species are slow growth, shallow root system, and small biomass production and the biomass must be disposed properly after harvesting.

Phytostabilization is the most commonly used for the contaminated soil, sediment and

sludge remediation. It can deal with the reducing of the mobility and bioavailable of contaminants in soil by their stabilization. This method utilizes the certain plant species to block the contaminants through the sorption, precipitation, complexation processes by the roots of plants immobilization. Thereafter, the mobility of contaminants is reduced and prevented to migrate to the ground water and the food chain. A dense root system which is metal-tolerant species stabilized the soil, decreased the potential migration of pollutants and prevented erosion (Ghosh & Singh, 2005; ITRC, 2009). This technique is useful for the remediation of Pb, As, Cd, Cr, Cu and Zn (Mahar et al., 2016). However, this technology contains several major disadvantages such as contaminants remaining in the soil after treatment, therefore, the mandatory monitoring is required.

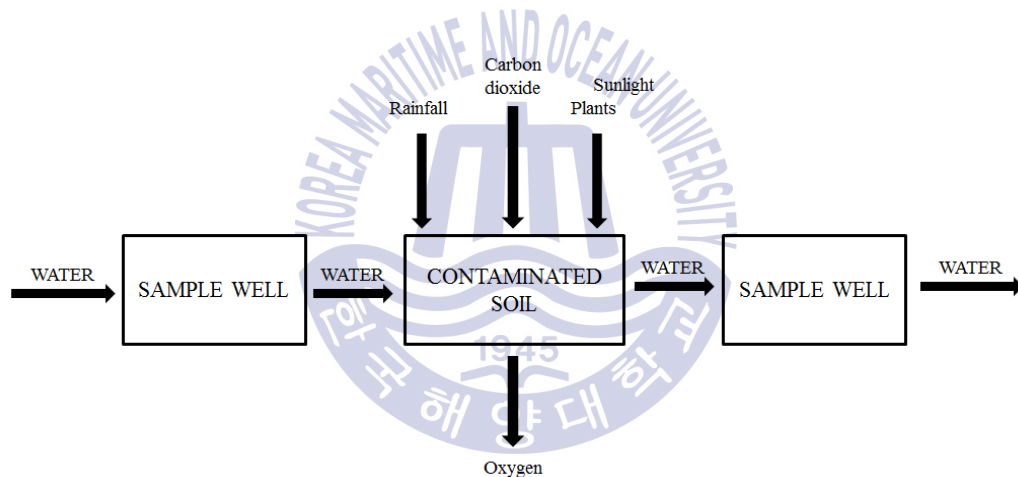


Fig. 2.2 A typical process diagram of phytoremediation (Vasavi et al., 2010).

Some of the advantages and disadvantages associated with phytoremediation technology are summarized in table 2.2. Even though phytoremediation shows significant advantages in the potential of contaminated soil treatment, it is still facing with considering disadvantages as the range of heavy metal concentrations which could be applied is very narrow. Furthermore, the period needing to clean-up sites by plants is even several years and it depends on the weather aspects and climatic conditions (Etim, 2012).

Table 2.2 Main advantages and disadvantages of phytoremediation

Advantages	Disadvantages
Metal contaminants are permanently removed from the soil after treatment.	Limited by slow growth of plants for contaminant accumulation and it takes many growing seasons to clean up a site. The depth of treatment is limited, in-situ 1-2 m deep, 3-5 m deep treatment possible only with special design.
The plants in the contaminated site can be easily monitored.	
Phytoremediation is the least harmful method for human health because it uses the natural material.	Phytoremediation is not effective for high content of contaminants or strongly-sorbed contaminants (poly-chlorinated biphenyls).
Relatively inexpensive when compared to conventional methods.	Plants that absorb toxic materials could be a problem for treatment after harvesting.
Planting vegetation on a site also reduces erosion by wind and water.	Scientists need to establish the regular monitors to determine the fate of toxic compounds in the plant metabolic cycle.
Can remove the contaminants from soil and isolate them without destroying the soil structure.	Degradation of by-products after phytoremediation could be mobilized in groundwater and accumulated in animals.

Phytoremediation is an interesting method which has been studied by many researchers and widely applied for many commercial contaminated sites. However, the ability to remove and accumulate metals of plants varies significantly and depends on many factors such as growth rate of plants, element selectivity, methods of harvesting. Furthermore, soil pH is a major factor influencing the availability of heavy metals in its formation in soil and supplying the growing condition for plants (Burlakovs, 2015; Mahar et al., 2016).

2.2.2. Stabilization/solidification technology

Stabilization/Solidification (S/S) (Fig. 2.3) is one of the promising methods for contaminated remediation, which is defined as a chemical treatment process that aims at immobilizing hazardous compound stream by converting them into a less soluble form, inert material and encapsulating them with the creation of durable matrix (Paria and Yuet, 2006; Kogbara, 2013). The technology also aims at keeping the hazardous components, minimizing the rate of contaminant migration into the environment, decreasing the surface area of the pollutants which can transfer or leach, and reducing the toxicity. S/S treatment method involves both of chemical fixation and physical encapsulation processes: (1) stabilization of the pollutant bonding environment via chemical transformation, (2) solidification of the contaminant by physical encapsulation (Paria and Yuet, 2006). S/S which requires the addition of a binding agent, is usually conducted by the combination of contaminated sludge and various types of binders, additives and chemical such as inorganic binders (e.g., Portland cement, lime/fly ash, and cement/fly ash, gypsum, etc. (Ba-Naimoon & Hamid, 2016)), and organic binders (e.g., asphalt, epoxy, organophilic clays, polyesters, granulated activated carbon, and polyethylene). Conventionally, the stabilizers using lime and cement were used for S/S treatment. However, with the utilization of waste materials having cementing properties, the materials become more widely. The combination of the inorganic binders and organic binders has been used. However, the inorganic binders are generally less expensive than organic binders and easier to apply.

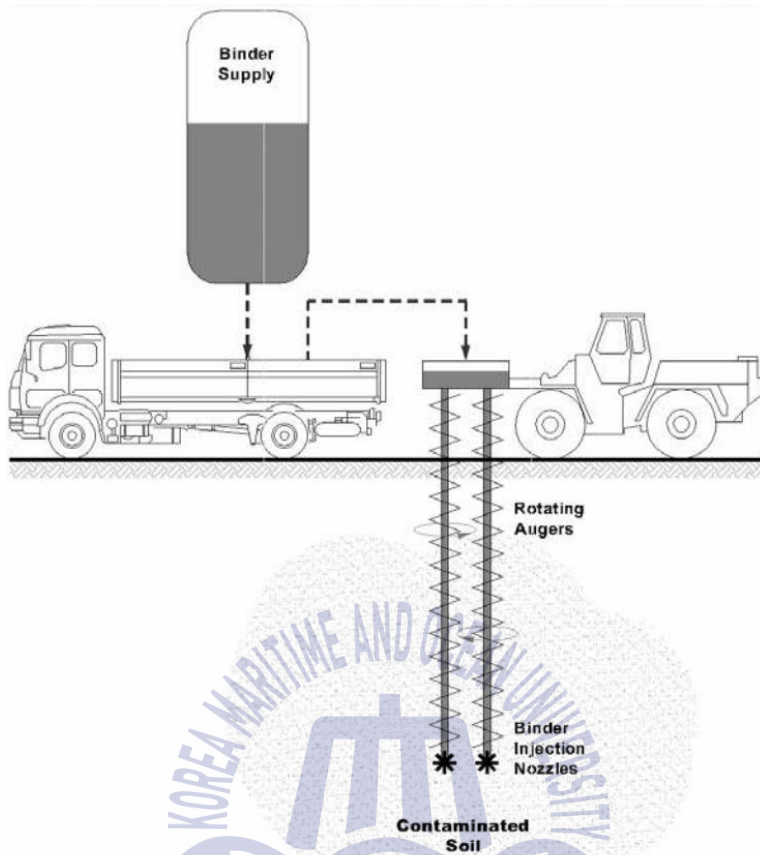


Fig. 2.3 Stabilization/Solidification technology for remediation using binders.

According to Tuncan and his coworkers (2000), the use of cement, fly ash, and lime with the addition of 5%, 10%, and 20% could increase the strength of the cemented product. The *in-situ* S/S involves various methods to mix the binding reagent and contaminated media, the immobilization of contaminants, as well as binding mechanisms, depends on their nature. However, there are three main mechanisms could be listed:

1. The sorption occurs when adding a solid (hydration products) to contaminants, make the interaction between them. It is also called chemical fixation.
2. Physical trapping of the contaminants on the surface of cement hydration products to produce the high strength waste/concrete matrix by using the combination of pozzolanas, fly ash, non-crystallize silica and the calcium in lime.

3. Physical encapsulation of pollutants with melted asphalt or similar materials.

Once happens when the binder is applied through the nozzles of the augers at the bottom. Then, they turn, mixing and drilling into the contaminated soil (Fig.2.3).

Turning to the process types, there are various S/S processing schemes available can be applied (Wiles, 1987):

1. In-drum processing: in this process, the wastes contained in a drum or different kinds of containers are added by the S/S binders. The waste-binder matrix after mixing is then disposed of in the drum.
2. In plant processing: this technology is usually used for special purpose such as solidification/stabilization of bulk waste material. The waste from an internal industrial operation, or a plant operated to solidify/stabilize waste from external sources.
3. Mobile plant processing: this scheme refers to S/S processes and equipment which are easily mobilized or transported and set-up site to site.
4. *In-situ* processing: binders or the injection of solidifying/stabilizing materials are directly added to promote the solidification/stabilization of the contaminated sludge or soil.

The advantages and disadvantages of S/S treatment method vary with many factors such as type of process, kind of blinder, contaminant, and site conditions. The table below presents some main advantages and disadvantages.

Table 2.3 Summary of advantages and disadvantages of S/S method

Advantages	Disadvantages
Relatively low cost because the reagents are widely available and cheap, ease of use and processing.	The total volume of contaminated soil after treatment will be increased significantly (Wiles, 1987).
Long-term stability, both in physical and chemical.	Hazardous waste remains in soil, it could not be removed from site.
Could be employed to different types of contaminant, comprehensive strength.	<i>In-situ</i> S/S process is more complex than other types of process by delivering reagents deep into the waste and mixing them.
High resistance to be biodegraded.	The extensive transportation of the waste materials takes place in some situations.
Could be applied on a large variety of pollutants.	Long-term efficiency of S/S treatment method is still uncertain and need to be regularly monitored (Burlakovs, 2015).
Equipment is widely available and simple.	Volatilization of organic compounds and some particulates may come out during treatment process.

2.2.3. Bioremediation

Bioremediation is an alternative treatment technology in which the hazardous compounds are destroyed and transformed into the simple inorganic compounds or less toxic forms with the use of microorganism, organisms (bacteria, fungi or plants) by ionic exchange mechanism (Vidali, 2001). Bioremediation approach has been proven as an effective, low-cost, environmentally-friendly treatment option due to the biodegradable products after treatment. Furthermore, this technology shows a lot of advantages such as simple to maintain, complete destruction of the contaminants (Bento et al., 2003; Robles-González et al., 2008). Microorganisms have the ability to accumulate the heavy metals from polluted sources with several mechanisms such as physicochemical phenomenon which also involves the energy production via redox reaction within microbial cells (Adams et al., 2015). It also demonstrated the capability to transform and uptake the heavy metals from contaminated site and proved many ways to transport the heavy metal through the cell membrane, biosorption to cell walls and entrapment in extracellular capsules, micro-precipitation, and complexation (Veglió et al., 1997). The efficient bioremediation performance depends on physical and chemical factors including contaminant concentrations, contaminant bioavailability, site characteristics such as water, temperature, pH as well as other ions in solution and it can be useful only where the environmental conditions are suitable with the microbial growth and activities (Adams et al., 2015).

Bioremediation processes have been classified in both *in-situ* and *ex-situ* remediation techniques which *in-situ* involves leaving the soil in its original site with minimal disturbance. Otherwise, *ex-situ* involves digging and removing the soil from the contaminated site with the imported microorganisms from external place to enhance the degradation process.

Table 2.4 General types of Bioremediation

Bioremediation	<i>In-situ</i>	Bioventing	<p>Injecting air and nutrients into the contaminated media through the wells to stimulate the indigenous bacteria.</p> <p>Allowing for the treatment of less permeable soils due to low air flow rates are required (Baker & Moore, 2000; Lee & Swindoll, 1993).</p>
		Biosparging	<p>The injection of atmospheric air under pressure to move the air to the unsaturated soil zone, then enhance the rate of biological degradation of contaminants (Kumar et al., 2011).</p>
		Bio-augmentation	<p>With the addition of microorganisms indigenous or exogenous to the polluted sites. However, the exogenous microorganisms could not adapt easily in the new environment and the well management is required (Kumar et al., 2011).</p>
	<i>Ex-situ</i>	Landfarming	<p>The contaminated soil is excavated and spread on the ground surface with the addition of nutrients, minerals and moisture for aerobic microbial activity (Khan et al., 2004).</p>
		Biopiles	<p>Biopile cells are constructed into the piles or heaps by aeration with the addition of minerals, nutrients and moisture to stimulate the microbial activity. The piles which supply air from underground system could be up to 6 m high (Khan et al., 2004).</p>

		Bioreactors	Decomposing processes are fulfilled in a closed container by attrition and mixing the contaminants, nutrients, air, microorganism and moisture. Bioremediation rate of bioreactors is higher than <i>in-situ</i> techniques because the environment in container is more manageable and easier to control (Kumar et al., 2011).
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Table 2.5 Summary of main advantages and disadvantages of Bioremediation treatment

Advantages	Disadvantages
Bioremediation is a natural process and is therefore more acceptable for contaminated treatment than other methods.	In-situ treatment is limited by the depth of soil and the range of contaminants is limited to remove effectively.
Low-cost technology, more economical than other conventional methods.	Some contaminants such as chlorinated organic/high aromatic hydrocarbons are resistant to microbial attack.
Could be used for wide variety of contaminants in which after treatment, the hazardous compounds will be degraded to harmless products such as water, carbon dioxide, and cell biomass.	Time scales are relatively long for the treatment, usually several months to achieve acceptable levels, longer than other treatment options such as soil washing or incineration.
The complete destruction could be done instead of transferring from contaminated soil to the water environment or air.	When the additives are added to enhance the biodegradation rate, other organisms could be disrupted.

	<p>Because the hazardous compounds in soil are not usually homogeneous, therefore not all compounds are complete degradation in treated time. Sometimes, the products are more persistent or toxic than parent compound.</p>
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2.2.4. Soil washing

Soil washing became one of the most interested technologies for contaminated remediation tool that has employed a number of physical separation and/or chemical extraction processes to extract several types of contaminants from soils. Soil washing refers to *ex-situ* technique in which washing solution (water or combination of chemical additives) was used to scrub the soil, separate the contaminants from pollutant-soil matrix, and then the clean soil and wastewater was separated by filtration (Griffiths, 1995; Yao et al., 2012). Schematic diagram of typical options used for soil washing was illustrated in Fig. 2.4 with processes: option 1 – physical separation, option 2 – chemical extraction, and option 3 – combination of both (Dermont et al., 2008). Heavy metals in soil can exist in many forms such as discrete particles, metal-bearing particles, or adsorbed species. Therefore, the appropriate remediation technology for metal removal is very much affected by contaminant characteristics.

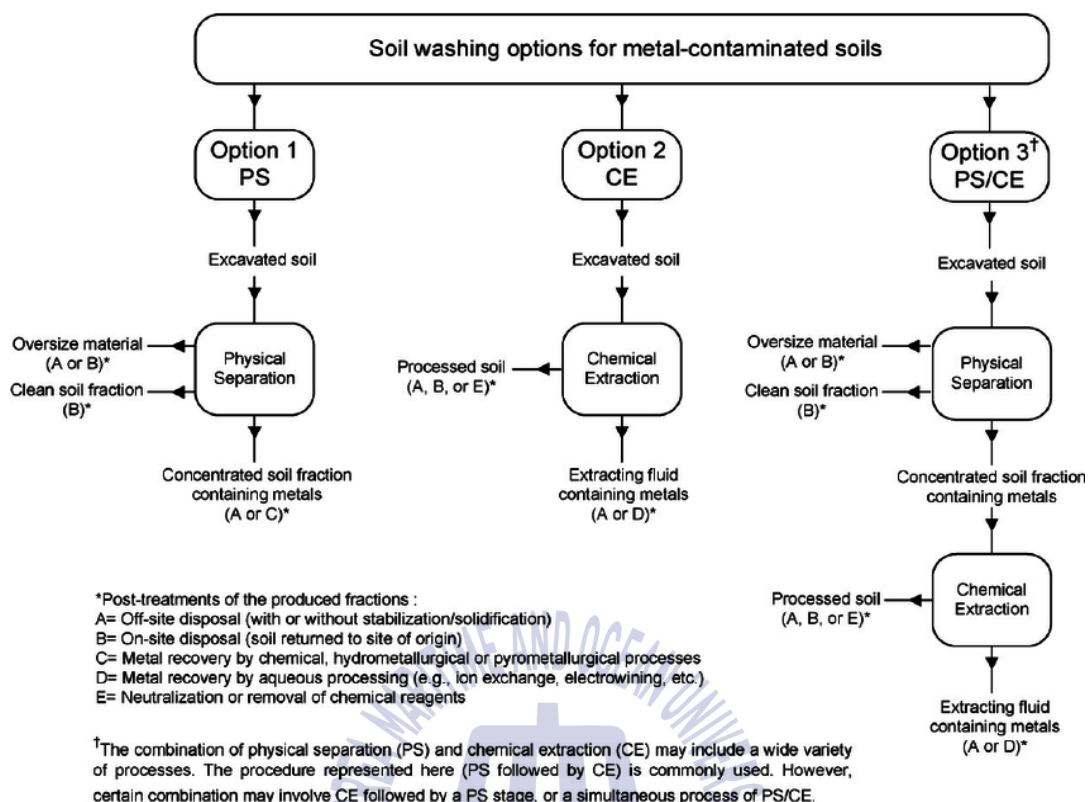


Fig. 2.4 Schematic diagram of typical options used in soil washing processes
 (Dermont et al., 2008)

2.2.5. Physical separation

In this section, physical separation is primarily mentioned as a method to concentrate metal contaminants from the contaminated area to a smaller volume which is based on the differences of physical characteristics between the metal-bearing and soil particles. This technique which has been employed widely in mineral processing and mining industries for several years, provides background information for the physical separation of particles from each other (USEPA, 1995). The contaminated liberation of this *ex-situ* method depends on several factors: contaminant forms/characteristics, soil particle size distribution, shape, hydrophobic properties of particle surface, or the differences of densities between soil matrix and heavy metals. Therefore, it refers to treat the discrete particles of heavy

metals or metal-bearing particles more than metal-sorbed forms or metal contaminants strongly bound on soil surfaces (Battelle, 1997). Physical separation has been classified to several techniques, which depends on their separation principles: hydrodynamic classification, gravity concentration, froth flotation, attrition scrubbing, and magnetic separation. The table 2.6 below summarizes the main physical separation technologies for contaminated remediation with the basic principle and technology description.

Table 2.6 Summary of physical classification options

Technique	Basic principle	Advantages	Limitations
Hydro-dynamic separation	Main target of hydro-classification is particle size separation. Different settling velocity or separation by centrifugal force makes the different settling rates (USEPA, 1995).	Time for separation by centrifugal force is much less than gravity separation. Simple, inexpensive equipment and operational costs.	Not useful when applied for fine particle separation. Screens can plug and fine screens are fragile.
Gravity separation	Rely on a density differences between the phases of heavy metals and soil. The separation efficiency depends on particle size, different density, fluid viscosity and particle concentration (Battelle,	Simple equipment and low cost operation. Possibility and cheapness for different ranges of size separation (0.1 – 300 mm).	Inefficient when used to treat particles have wide range sizes and narrow density distributions (USEPA, 1995).

	1997; GWRTAC, 1997).		
Froth flotation	<p>Contaminants are separated due to the differences of hydrophobic properties of particle surfaces and soil matrix.</p> <p>Particles are attached to bubbles and removed by flotation (GWRTAC, 1997; Dermont et al., 2010).</p>	<p>Surface properties can be altered depending on the flotation reagents.</p> <p>High efficiency with the fine particles.</p>	<p>Only effect with the low concentration of the particulate.</p> <p>Complex, expensive treatment method and could be influenced by slime.</p>
Magnetic separation	<p>Separation based on the ferromagnetic materials associated with contaminants or the differences between the magnetic properties of particles (Dermont et al., 2010; Battelle, 1997).</p>	<p>With both of low and high intensity of magnetism separation, these methods can recover variety of materials.</p> <p>Effective recovery of ferrous minerals from nonferrous minerals, portable and powerful.</p>	<p>Should be maintained consistently, regularly washed or wiped.</p>

Even though physical separation is a simple technology, it has approved several advantages: (1) it can be used for both of inorganic such as metal contaminants and organic

compounds in the same treatment system; (2) after treatment, the volume of soil for off-site disposal or metal recovery reduced; (3) the treated soil can be returned in site after treatment with low cost; (4) with high concentration of metals after treatment could be sent for recycling; (5) the technologies are very well established in the mineral processing industry and the operational costs are usually low (Burlakovs, 2015). However, physical classification is not suitable for treating the sorbed form of metal with soil particle as well as the silt or clay percentage in contaminated site is high (Dermont et al., 2008). In these cases, physical separation is often followed by other methods for effective removal such as chemical extraction, which will be presented below.

2.2.6. Chemical extraction

The combination of physical separation and chemical extraction, in which physical separation concentrates the contaminants into a small volume due to the coarse metal particles have been removed from the bulk soil; and followed by chemical method which plays a role as an extractant to dissolve the metals and transfer it from the solid phase to liquid phase. Chemical extraction is a method that employs the extracting fluid with water-based system (acids/bases, chelating agents, surfactants or redox agents) to dissolve the metals from soil into solution. This process applies for the contaminants with ionic metals formed with soil proportions (adsorbed form). Solubility of metal in solution could be enhanced by dissolving or converting the metal compounds into more soluble forms (Dermont et al., 2008; Yao et al., 2012).

Several chemical reagents have been studied on metal removal such as acids, high-concentration chloride salt solutions, chelating agents, surfactants, and redox agents with different dissolved mechanisms (Yang et al., 2005; Wuana et al., 2010; Tessier et al., 1979; Peng et al., 2005).

- (1) pH solution changes (by acid reagents).

- (2) System ionic strength changes (by addition of salts).
- (3) Formation of metal complexes (by addition of chelating agents).
- (4) Changes in redox potential (with addition of reducing or oxidizing agents).

Solubilization efficiency of metals depends on many factors including soil geochemistry (e.g. soil texture, cation exchange capacity, buffering capacity, and organic matter content); metal contamination characteristics (type of contaminant, valence of ionic metals, concentration, speciation of metals); dosage and extracting agent; and leaching conditions (pH solution, leaching time, liquid/solid ratio, and mode of reagent addition) (Dermont et al., 2008). In this study, the review of acid leaching, chelating extraction, redox agents, and surfactant-enhanced solubilization are mentioned in this table.

Table 2.7 Summary of chemical extraction options

Technique	Basic principle	Advantages	Limitations
Acid leaching	Acid leaching involves inorganic acids (H ₂ SO ₄ , HCl, HNO ₃ , etc.) or weak organic acids (acetic acid) which can supply proton H ⁺ . Under the low pH condition, the extraction mechanisms of metal include: + Desorption of metal cations via ion exchange.	+ Has been proven as an effective removal method and become commercial scale. + Permanent treatment to remove the metals from soil. + Inorganic acids are cheap and could be widely applied in full scale.	+ Acid leaching can destroy the soil structure, organic matter, soil mineral substances as well as soil microbiology. + The treated soil could be acidified by using strong acid. + Wastewater and treated soil need to be neutralized. This process also

	<p>+ Dissolution of metal compounds.</p> <p>+ Dissolution of soil mineral components (Fe-Mn oxides) (Ko et al., 2005).</p>		<p>generates enormous amount of toxic compounds (Peng et al., 2005; Tampouris et al., 2001; Stylianou et al., 2007).</p>
Chelating extraction	<p>The metal removal is based on the stable complexes between chelating agent and metal.</p> <p>The selection of chelating agents is based on these factors:</p> <ol style="list-style-type: none"> (1) Highly stable complexes in a wide pH range. (2) Metal complexes should not be re-adsorbed on soil surfaces. (3) Chelating agents can be recycled for reuse. (4) Should be cost 	<p>Chelating agents cause less destruction of the soil structure than strong acids.</p> <p>Environmentally-friendly approach</p> <p>Chelating agent such as EDTA shows the most effective reagent: strong chelating ability with metals, forming the stable complexes with metals in wide pH range, recoverable and reusable, and high thermal resistance (Yin et al., 2014).</p>	<p>Chemical reagents are expensive compared with inorganic acids.</p> <p>The low biodegradability degree causes the mobile potential of metal in soil.</p>

	<p>effective.</p> <p>Metal recovery is possible (Dermont et al., 2008; Doumet et al., 2008).</p>		
Redox agents	<p>Redox agents can enhance the solubility of metal-sorbed form based on their chemical-oxidation/reduction potential.</p>	<p>Enhance the metal removal efficiency by degrading variety of hazardous compounds or transferring metals into more soluble form. Could be conducted in both in-situ and ex-situ.</p>	<p>Not suitable for low permeability soils such as clay.</p> <p>Just applicable to contaminants that can be oxidized or reduced (Goi et al., 2009; U.S. DOE., 1999).</p>
Surfactants	<p>Heavy metal removal from the soil by using surfactant is mainly based on the surfactant-associated complexation and ionic exchange due to their sorbed-form on soil surface (Mao et al., 2015). It also has been studied to</p>	<p>Large quantity of soil do not need to be excavated and handled by using surfactant treatment. Biosurfactants have not only capability to desorb and dissolve the contaminants, but also are environmentally-friendly agents (Mao et al., 2015).</p>	<p>The fate of added surfactant needs to be concerned.</p> <p>It is ineffective to treat the soil with low permeability, heterogeneity and extremely insoluble metals.</p> <p>The price of surfactants is</p>

enhance the complexation agents or redox agents when aiming at assisting desorption/dispersion of metal from soil surface (Mulligan et al., 2001).		expensive compared with other agents. Therefore, it is limited to become a massive production (Mao et al., 2015; Mulligan et al., 2001).
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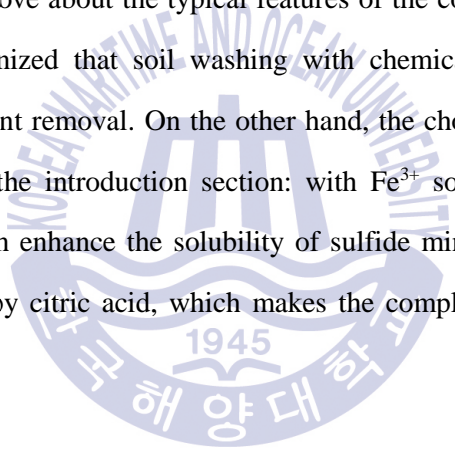
2.3. Typical features of contaminated soil and decision tools for remediation planning

Table 2.8 Appraisal of option for choices

Typical features of tailings	
The particle size from abandoned mine is very fine ($< 75\mu\text{m}$).	Not suitable for the use of gravity separation technique.
Mine tailings with variety of contaminants with high level of metal content.	Not suitable for the use of phytoremediation or bioremediation which needs long-term treatment, and physical separation.
Mine tailings usually present with contaminants in metal-sorbed form.	Not suitable for the use of physical separation in full-scale, which prefers contaminants in liberated metals (particular forms).
Arsenic (As) and other heavy metals are often in form of sulfide minerals such as pyrite (FeS_2), arsenopyrite	Not suitable for bioremediation treatment.

(FeAsS), chalcopyrite (CuFeS ₂), etc.	
	<p>Furthermore, these limitations needing to be considered:</p> <p>Not suitable for the use of strong acid treatment due to the consequent environmental issues</p> <p>Not suitable for the use of surfactants in full-scale due to the high-cost treatment method.</p>

With the given table above about the typical features of the contaminated soil from this study, it has been recognized that soil washing with chemical extraction is the most appropriate for contaminant removal. On the other hand, the choice of chemical additives is already mentioned in the introduction section: with Fe³⁺ solution plays a role as an oxidative agent which can enhance the solubility of sulfide mineral forms into the more soluble forms, followed by citric acid, which makes the complexes with liberated metal ions in the solution.



Chapter 3 Sequential Extraction

3.1. Materials and sample characteristics

The tailing samples in this study collected from a confidential abandoned mine site in Korea which were contaminated by very high level of heavy metals. The soil surface was gathered, air-dried and sieved with 75 μm sieve to remove coarse gravel, debris, and pebble, and it showed the dark-gray coloration. Samples were homogenized and stored in the plastic container for subsequent experiments. The chemical composition of sample was obtained by using aqua regia digestion. The digested solution was filtered, and the chemical components of sample were identified by OPTIMA 8300 DV inductively coupled plasma-atomic emission spectrometry (ICP-AES, PerkinElmer Inc., USA). Due to the mining activities, it showed that the soil was heavily contaminated by Fe, As, Mn, Zn, Cu, and Pb. The table of content analysis indicated that total concentrations of heavy metals from this mine tailing are very high, especially with Fe, As, Mn containing 28.89 %, 11.83 %, and 9.02 % in bulk sample. Furthermore, the XRD pattern of the soil sample using Cu-K β radiation source shown in Fig. 3.1 also proved that except SiO₂, mostly the metal forms were found in metal sulfide minerals with arsenopyrite (FeAsS), pyrite (FeS₂) and arsenic trisulfide (As₂S₃).

Table 3.1 Chemical composition of the soil bulk

Element	Fe	As	Mn	Zn	Cu	Pb
Content (%)	28.89	11.83	9.02	1.82	1.65	1.74

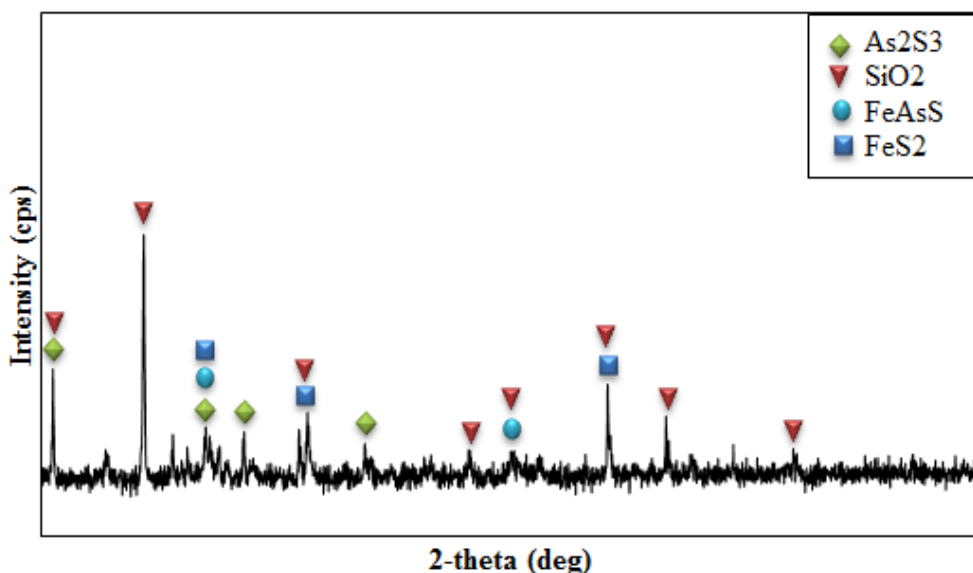


Fig. 3.1 XRD pattern of tailing sample.

3.2. Sequential extraction procedure

There are several approaches which used to determine the chemical distributions of the soil or sediment. The use of extraction reagents to selectively leach the specific geochemical phases is very important for sequential extraction procedure design. In present study, the soil samples were subjected to the sequential leaching procedure proposed by Tessier et al. (1979) and followed by Park et al. (2013). In this study, 1.0 g dried soil sample, which was suggested by Tessier's, and 0.2 g soil by author were carried out simultaneously. Metal speciations involved following five fractions: exchangeable (1), bound to carbonate (2), bound to Mn-Fe oxides (3), bound to organic matter (4) and residual (5) compatible with five steps:

Step 1 (1): 8 mL of 1 mol/L magnesium chloride (MgCl_2) (adjusted to pH 7) in the shaking bath at room temperature for 1 h.

Step 2 (2): 8 mL of 1 mol/L sodium acetate (CH_3COONa) (adjusted to pH 5) in a shaking bath at room temperature for 5 h.

Step 3 (3): 20 mL of 0.4 mol/L hydroxylammonium chloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) (in 25 % CH_3COOH) in a heating block at 96 °C for 6 h.

Step 4 (4): This extraction was divided into three phases, (i) 3 mL of 0.02 mol/L nitric acid (HNO_3) and 5 mL of 30 % hydrogen peroxide (H_2O_2) (adjusted to pH 2) in a heating block at 85 °C for 2 h. (ii) It then followed by 3 mL of 30 % H_2O_2 (adjusted to pH 2) in a heating block at 85 °C for 3 h. Finally, (iii) 5 mL of 3.2 mol/L ammonium acetate ($\text{CH}_3\text{COONH}_4$) (in 20 % HNO_3) and after cooling about 1 h in room temperature, about 4 mL deionized water was added and agitated continuously in the shaking bath at temperature for 30 min.

Step 5 (5): 20 mL aqua regia digestion was introduced in the extraction of the residual fraction for 20 min at 90 °C and 200 rpm agitation speed.

After each step of sequential extraction, the solid/liquid was separated by centrifugation at 5,000 rpm for 15 min, and then the designated amounts of supernatant were taken out by syringe, then solution was filtered with a 0.45 μm membrane filtered and diluted with 2 % HNO_3 solution. The concentrations of heavy metals Fe, As, Mn, Zn, Pb, Cu in each fraction of both 1.0 g and 0.2 g soil constituted in supernatant were analyzed using OPTIMA 8300 DV inductively coupled plasma-atomic emission spectrometry (ICP-AES, PerkinElmer Inc., USA). The residue after each step filtration was used in subsequent steps after washing two times by centrifugation with 20 mL deionized water. The data set was repeated triple times and each data point in an average of three repeats.

3.3. Chemical distribution of metals in Mine Tailings by Sequential Extraction.

Table 3.2a and 3.2b below gave us the information about the metal contents of Fe, As, Mn, Zn, Pb, and Cu, including mg/kg tailings, percentage of total content obtained of five steps sequential extraction, with 3.2a mentioned 1.0 g soil and 0.2 g soil sample for 3.2b. Corresponding with the table results above, the distribution of each fraction from sequential extraction for Fe, As, Mn, Zn, Pb and Cu was mentioned in Fig. 3.2a (1.0 g soil) and Fig. 3.2b (0.2 g soil).



Table 3.2a Results of sequential extraction of mine tailings, given in mg/kg tailings, and % of total content in five steps with 1.0 g soil sample followed Tessier suggestion

Step (Fractionation)	Metals	Fe	As	Mn	Zn	Pb	Cu
1. Exchangeable	mg/kg tailings	291	209	1,597	126	54	175
	Proportion (%)	0.10	0.19	1.74	0.89	0.34	1.11
2. Bound to carbonate	mg/kg tailings	1,272	176	4,545	452	1,766	1,166
	Proportion (%)	0.44	0.16	4.95	3.18	11.06	7.39
3. Bound to Mn- Fe oxides	mg/kg tailings	19,441	306	57,176	470	1,173	1,410
	Proportion (%)	6.79	0.27	62.29	3.31	7.35	8.94
4. Bound to organic matter/sulfide mineral	mg/kg tailings	20,639	1,870	4,765	3,388	4,124	2,259
	Proportion (%)	7.20	1.68	5.19	23.86	25.83	14.32
5. Residual	mg/kg tailings	244,838	108,743	23,702	9,762	8,849	10,760
	Proportion (%)	85.46	97.70	25.82	68.76	55.43	68.23
Total content	mg/kg tailings	286,481	111,304	91,785	14,198	15,965	15,770

Table 3.2b Results of sequential extraction of mine tailings, given in mg/kg tailings, and % of total content in five steps with 0.2 g soil sample followed present study

Step (Fractionation)	Metals	Fe	As	Mn	Zn	Pb	Cu
1. Exchangeable	mg/kg tailings	2,187	279	1,988	120	139	133
	Proportion (%)	0.77	0.25	2.11	0.80	0.81	0.71
2. Bound to carbonate	mg/kg tailings	2,227	156	15,384	479	1,987	865
	Proportion (%)	0.79	0.14	16.31	3.19	11.63	4.59
3. Bound to Mn-Fe oxides	mg/kg tailings	29,453	661	72,303	1,336	1,542	2,704
	Proportion (%)	10.42	0.58	76.65	8.90	9.02	14.33
4. Bound to organic matter/ sulfide mineral	mg/kg tailings	86,636	31,202	2,573	7,715	4,572	9,529
	Proportion (%)	30.65	27.60	2.73	51.36	26.75	50.50
5. Residual	mg/kg tailings	162,131	80,751	2,079	3,758	8,851	5,637
	Proportion (%)	57.36	71.43	2.20	25.02	51.79	29.87
Total content	mg/kg tailing	282,633	113,633	94,330	15,022	17,091	18,868

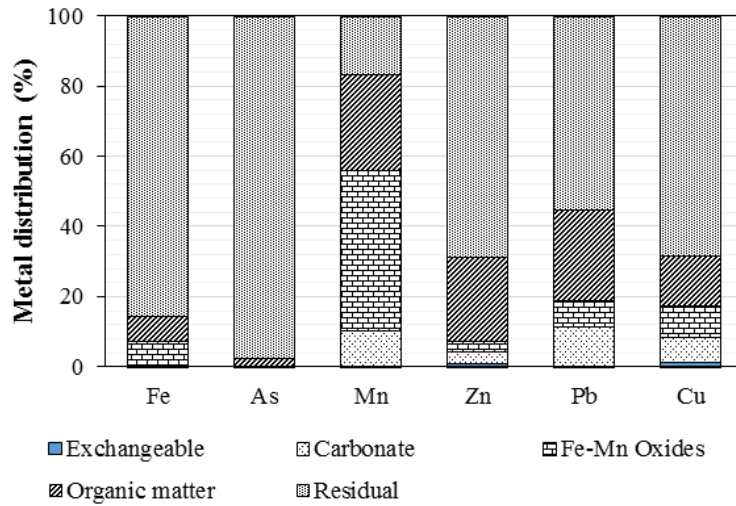


Fig. 3.2a Chemical distributions of Fe, As, Mn, Zn, Pb, and Cu in sequential extraction with 1.0 g soil sample followed Tessier's suggestion.

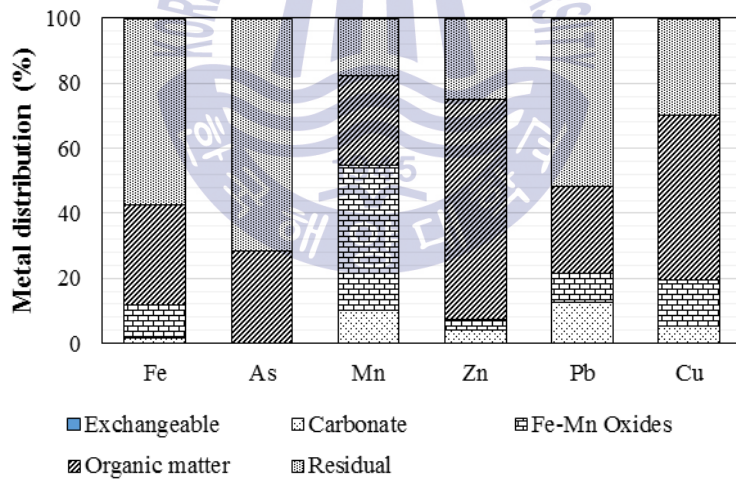


Fig. 3.2b Chemical distributions of Fe, As, Mn, Zn, Pb, and Cu in sequential extraction with 0.2 g soil sample followed present study.

As can be seen in 1.0 g soil sample suggested by Tessier's procedure, the highest portion was residual fraction with Fe – 85.46 %, As – 97.7 %, Zn – 68.76 %, Pb – 55.43 % and Cu – 68.23 %, respectively. It was also observed that the highest portion with 0.2 g soil led to change to bound to organic matter and sulfide minerals fraction with Zn – 67.59 % and Cu – 50.50 %, respectively. On the other hand, the significant amounts of metal content from residual fraction in 1.0 g soil sample moved to other portions (bound to Mn-Fe oxides and bound to organic matter and sulfide minerals), which were shown Fig. 3.2a and Fig. 3.2b. These results hence could be explained due to very high content of metals in soil sample, the operating conditions followed by Tessier's scheme led to incomplete dissolution of metal soil phases. For this reason, it suggested that with the use of less sample (0.2 g) will obtain the exact information about the chemical forms when the high level of metals. Therefore, the application of 0.2 g soil will be chosen for the sequential extraction results. The results, furthermore, indicated Fe, As, and Pb were very stable and mobilize harder than other metals, which found in the residual fraction as the highest portion. It also could be observed that most of the content of Mn was bound to Mn-Fe oxides in both 1.0 g soil and 0.2 g soil, respectively.

3.3.1. Exchangeable fraction

Extracted metals in the exchangeable fraction are weakly-sorbed metal species, which could be released from the soil by soft extractants through ionic exchange leaching processes and are usually retained on the soil surface by weak electrostatic interaction (Gleyzes et al., 2002; Rauret, 1998). Among several reagents for this extraction procedure (e.g. NH_4NO_3 , NH_4OAc , CaCl_2 , NaNO_3 , etc.), 1 mol/L MgCl_2 has been applied for the study that includes strong Mg^{2+} ion exchange capacity and complexing ability Cl^- . The table 3.2a and 3.2b showed that, in particular, the mobile fractions determined are similar in both cases with As 0.19 %, Mn 1.74 %, Zn 1.26 %, Pb 0.54 %, and Cu 1.11 % in 1.0 g sample and As 0.25 %, Mn 2.11 %, Zn 0.80 %, Pb 0.81 %, and Cu 0.71 % in 0.2 g sample

except 0.10 % and 0.77 % Fe in 1.0 g and 0.2 g sample. Although in an exchangeable fraction, it accounts the very low percentage of the total amount, metal concentrations in this fraction are still very high due to its high content of the contaminated soil. 0.2 g soil sample contained 2,187 mg/kg Fe, 279 mg/kg As, 1,988 mg/kg Mn, 120 mg/kg Zn, 139 mg/kg Pb, and 133 mg/kg Cu from the exchangeable fraction. The proportions of metals under magnesium chloride extraction followed As (0.25 %) < Cu (0.71 %) < Fe (0.77 %) < Zn (0.80 %) < Pb (0.81 %) < Mn (2.11 %). This fraction is an important factor from the environmental and health risk aspect. Because under the environmental conditions, the metals in this fraction could be easily leached out from the soil and tend to bio-accumulate and directly cause serious health effects. Therefore, the content of heavy metals in this fraction was carried out to compare with Korea contamination soil criteria. Table 3.3 showed that the concentration of As was much higher than Korean contamination criteria with 279 mg/kg mine tailing, the Cu concentration was higher than A area in both acting and warning thresholds, and Pb concentration was higher than A area in warning threshold. These results indicated that this mine tailing has potential to be greatly contaminated, therefore, need to be appropriately treated to prevent this contaminated potential.

3.3.2. Bound to carbonate fraction

The trace metals associated with this phase play a significant role in trace metal behavior (e.g., the dissolution of carbonate into soil has potential to increase soil pH and enhance the fixation of trace metals to carbonates between the metal cations and the carbonate unit cell incorporation (Mseddi et al., 2010)). The bound to carbonate fraction is also called mobilizable fraction, which has potential to be leached under the environmental conditions and pH changes. Among several reagents for the second fraction (e.g., buffered acetic acid/sodium acetate, EDTA, DTPA, unbuffered acetic acid), buffered acetic acid/sodium acetate to pH 5 solution is the most widely applied. By adjusting the pH solution to 5.0 that can release the remaining specifically exchangeable trace metals as well as the carbonate-

bound trace metals (Tessier et al., 1979; Leinz et al., 2000). In fact, moreover, the extraction of metals from carbonate fraction depends on several factors related to sample and leaching solution such as particle size, initial content, type of carbonates and amount of reagents used. The comparison between exchangeable fraction and bound to carbonate fraction showed that the metal bound to carbonate contents are higher than exchangeable metal contents. Especially, up to 16.31 % Mn was found in the acetic/sodium acetate extraction, corresponding with 15,834 mg/kg tailings (table 3.2b). The high concentration may result from the dissolution of manganous carbonate with the reduced state, and therefore it was not derived from Mn-Fe oxide-bound fraction, which means that Mn extracted can come from the dissolution of Mg/Ca carbonate minerals. The proportions of metals under buffered acetic acid/sodium acetate extraction followed As (0.14 %) < Fe (0.79 %) < Zn (3.19 %) < Cu (4.59 %) < Pb (11.63 %) < Mn (16.31 %).

Table 3.3 Metal content of heavy metals from exchangeable fraction in the mine tailings and compared to Korea soil contamination criteria (with acting and warning criteria)

Metal (mg/kg)	Exchangeable fraction content	Korean soil contamination criteria			
		Acting		Warning	
		A area	B area	A area	B area
Fe	2,187	NE	NE	NE	NE
As	279	15	50	6	20
Mn	1,988	NE	NE	NE	NE
Zn	120	NE	NE	NE	NE
Pb	139	300	1,000	100	400
Cu	133	125	500	50	200

(A area: farmland, ranch lot, school lot, park, etc. B area: factory, railway, highway, etc.)

NE: Not Established)

3.3.3. Bound to Mn-Fe oxides fraction

These secondary oxides are considered as the excellent scavengers of metals, which can present as coating mineral surfaces or fine discrete particles. Several reagents have been applied for metal extraction from Mn-Fe oxide phases, which contain both a reducing reagent and a ligand can make complexes with liberated ions in solution. In this study, hydroxylamine with 25 % HOAc medium was used due to the ability to dissolve several metallic oxides of hydroxylamine, and complexing properties of acetate ions. It is, however, criticized that these reagents was considered insufficient for the extraction of crystalline iron oxides (Arunachalam et al., 1996; Krasnodebska-Ostrega et al., 2001). For both of the table 3.2a and the table 3.2b showed that, respectively, 62.29 % and 76.65 % total Mn were found to be extracted, whereas only 6.79 % and 10.42 % total Fe were leached in the solution. These results showed that decreasing sample five times from 1.0 g to 0.2 g did not result significant change in extractable metals. It is demonstrated that the extraction of reducible manganese and iron oxides are completed. The percentage extractions for As, Zn, Pb, and Cu were 0.27 %, 3.31 %, 7.35 %, and 8.94 % for 1.0 g sample. For 0.2 g sample showed 0.58 %, 8.90 %, 9.02 %, and 14.33 % for percentage extractions of As, Zn, Pb, and Cu, respectively. On the other hand, it is well known that most of extractable Pb bound to Fe oxides in soils (Krasnodebska-Ostrega et al., 2001; Tipping et al., 1985). However, only 7.35 % total Pb in 1.0 g sample and 9.02 % total Pb in 0.2 g sample were found in this reagent. It can be explained that the amount of Fe oxide leached in three-step scheme is also very low (6.79 % and 10.42 % in 1.0 g and 0.2 g sample). It is, therefore, assumed that the fraction of Fe and Pb mostly associated with sulfide fraction or in crystalline from.

3.3.4. Bound to organic matter or sulfide mineral fraction

In the organic phases of trace metals, the complexation or bioaccumulation processes are seemed to be the primary source (Okoro et al., 2012). Metal elements can be formed with various organic compounds such as an organic coating on mineral particles, biotic detritus

or living organisms. Metallic pollutants in this phase are assumed to be more stable by decomposition process and to stay in the soil for a longer period compared with exchangeable, bound to carbonate, and bound to Mn-Fe oxides fractions. In fact, however, degradation or decomposition of organic matter can occur under the oxidizing conditions or decomposition processes (Okoro et al., 2012; Marin et al., 1997). Afterward, the soluble trace metals bound to sulfides may be extracted. Therefore, this fraction is assumed to be bound to organic matter or sulfide mineral fraction due to the organic fraction released in this oxidation step is considered to contain sulfide-bound metals. Indeed, the XRD pattern of tailing sample showed in Fig. 3.1 illustrated that except SiO_2 , the main components of the tailing which can be detected by XRD existed in sulfide forms. This result was also proven by containing 19 % by weight of S element in soil samples by XRF analysis.

Hydrogen peroxide in the nitric acid medium conducted by heating for several hours is the most commonly used for the extraction of metals associated in organic phase. In fact, even though the oxidation process of all organic forms may not be completed, the use of other reagents such as nitric acid used separately or hydrochloric acid combination or perchloric acids have been used as alternatives to dissolve sulfides effectively. However, the partial of silicate lattices can be attacked (Gleyzes et al., 2002; Okoro et al., 2012). As can be seen in the table 3.2a and 3.2b, levels of all metals in fraction 4 are significantly changed from the use of 1.0 g to the use of 0.2 g sample with the increasing percentages of Fe 7.20 % - 30.65 %, As 1.68 % - 27.60 %, Zn 23.86 % - 51.36 %, Cu 14.32 % - 50.50 %. The results can be explained due to the insufficiency of reagents to dissolve completely high content of metal sulfides in the case of 1.0 g soil sample. In the case of Mn bound to organic matter, the percentage decreased from 5.19 % to 2.73 % of total Mn due to the complete dissolution of Mn in oxide form and other previous fractions by using 0.2 g sample. These results clearly indicated that the use of 0.2 g sample could give the exact information of metal distributions of metal in this tailing sample.

3.3.5. Residual fraction

This fraction is considered as a potential long-term risk of toxic metals entering the biosphere due to the mineral containing metals in their crystal structure. The destruction of this fraction could not be achieved without the digestion of concentrated acids. In this study, the residue from bound to organic fraction was digested with HNO₃ – HCl mixture (aqua regia). The results from table 3.2a showed that except Mn, all metals found in fraction 5 presented highest proportions and they were significantly higher than those observed in preceding extractions with more than 50% of the total metal concentrations. However, the metal proportions were significantly changed from table 3.2a to 3.2b. The percentages of total metal concentration decreased drastically with Fe 85.46 % - 57.36%, As 97.70 % - 71.42 %, Mn 25.82 % - 2.20 %, Zn 68.76 % - 25.02 %, Cu 68.23 % - 29.87 %.

Even though there were differences of metal distributions between 1 g sample and 0.2 g sample, these values indicated that the amount of all metals except Mn leached are much higher in “bound to organic matter/sulfide minerals”, “residue” than in “bound to carbonate” and “bound to Mn-Fe oxides”. These results suggested us that with the use of an appropriate amount of sample for sequential extraction, we can assess the mobility and potential mobility of metals in the environment.

Chapter 4 Leaching test

4.1. Leaching procedure

The leaching tests were performed in a 500 mL three-necked Pyrex glass reactor with the heating mantle to maintain the desired temperature. The illustration of apparatus was mentioned in Figure 4.1. The reactor was fitted with a stirrer, a flux condenser was also equipped to the reactor with continuous water flow to avoid the evaporation solution loss at high temperature. In each subsequent leaching test, 200 mL leaching solution containing predetermined concentration of ferric chloride hexahydrate and citric acid monohydrate or sodium citrate tribasic dehydrate was used. Then, solution was heated to the required temperature. The effect of ferric concentration (0 – 3.0 M) combined with 1.0 M of citric acid was conducted to investigate the metal extraction behavior. This study was also performed to investigate the effect of with and without the presence of 1.0 M citric acid with ferric chloride solution media. After that, by adjusting the ratio of citric acid and sodium citrate, the solution pH was adjusted in the range from 0 to 2.0. Once the solution reached thermal equilibrium (30 °C - 90 °C), 0.25 – 1.0 % pulp density was added with the various value of agitation speed 200 – 600 rpm.

During the leaching test, 1.5 mL of solution was withdrawn at the desired time interval (5 – 180 min) by syringe and was filtered with 0.45 μm membrane filter. The filtrate was diluted with 2 % HNO_3 solution and the metal concentrations after leaching were then measured with ICP-AES and the leaching residue was also analyzed with XRD.

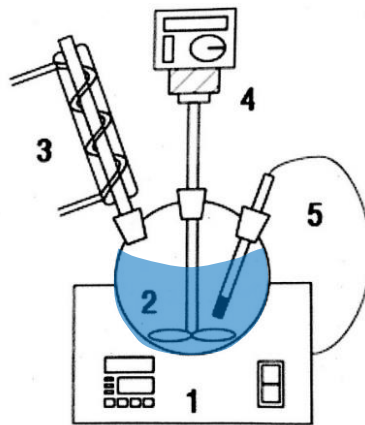


Fig. 4.1 Schematic diagram of the leaching apparatus

1. Heating mantle, 2. Reactor, 3. Condenser, 4. Agitator, 5. Thermometer

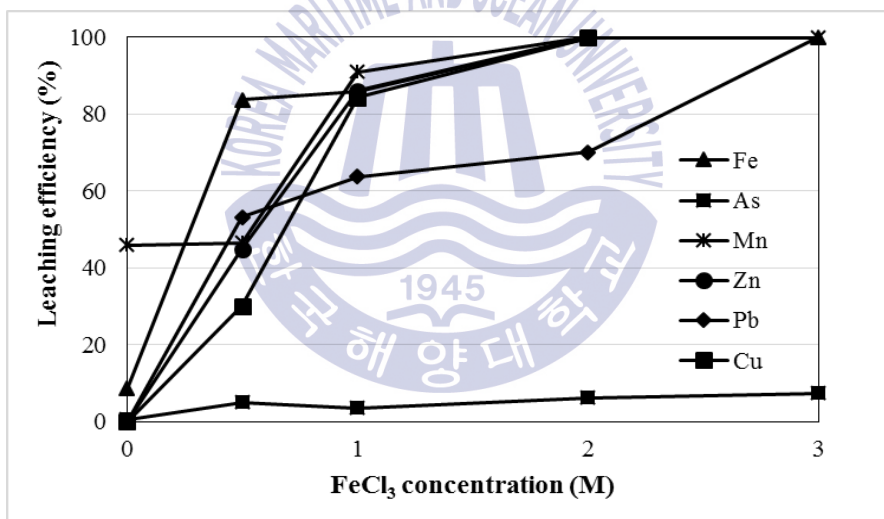


Fig. 4.2 Effect of initial ferric concentration on the extraction of metals (0-3.0 M Fe³⁺, 1.0 M citric acid, 50 °C, and 400 rpm with 3 h leaching time).

4.2. Results and discussion

4.2.1. Effect of ferric concentration

In this study, Fe^{3+} plays a role as the strong oxidant and the oxidation process of metal sulfides by Fe^{3+} could be depicted as followed equation



Where Me and Me^{2+} present metals such as Fe, Zn, Pb, Cu, and their ions, respectively.

Various values of ferric concentration (0, 0.5, 1.0, 2.0, 3.0 M) with 1.0 M of citric acid were carried out under the conditions of 50 °C solution temperature, 400 rpm agitation speed, 0.25 % pulp density and 3 h of reaction time. In this case, 0 M of Fe^{3+} means the leaching was conducted in 1.0 M citric acid solution without Fe^{3+} . At that point, Mn and Fe concentration were found at 45.9 % and 8.5 %, which matched with Park et al., (2013) that citric acid could leach metals in weathered forms such as carbonate or oxide-bound minerals. The leaching efficiencies of metals versus increasing ferric concentration were presented in Figure 4.2, which showed that the leaching efficiencies of metals increased with increasing ferric concentration. By increasing 3.0 M Fe^{3+} within 3 h reaction time, the reaction of Fe, Mn, Zn, and Pb reached the equilibrium with 100 % metal elements can be extracted in solution. As shown in Figure 3.1, the results could be explained that metals existed as sulfide forms, so with the increase of ferric concentration corresponding the increase of offered energy for breaking the bonds of chemical forms in metal sulfide compounds. However, the increase in As was not significant with 5.0 % in 0.5 M Fe^{3+} and 7.4 % in 3.0 M Fe^{3+} .

The mechanism of metal dissolution of sulfide minerals could be explained by the dissolution of metals by ferric ion first. After that, ligands increased mineral dissolution by adsorbing these chelating agents on mineral surfaces or making complexes with liberated metal ions from solution, which were illustrated in Figure 4.3.

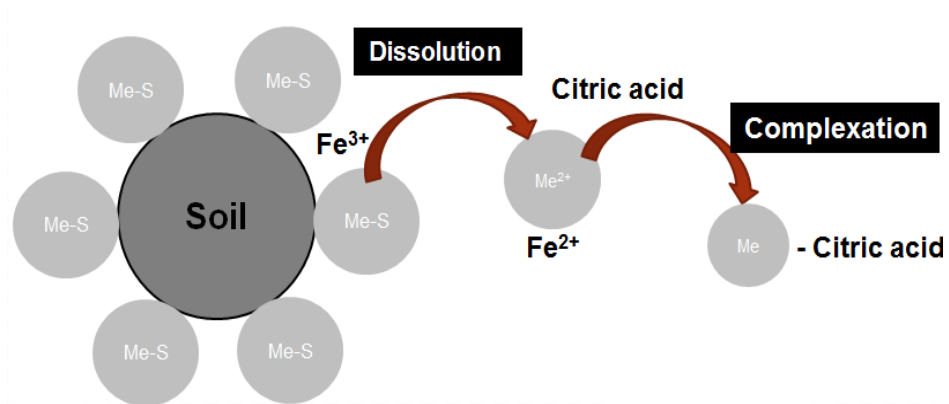


Fig. 4.3 Dissolution mechanism of sulfide metals under ferric ion and citric acid combination.

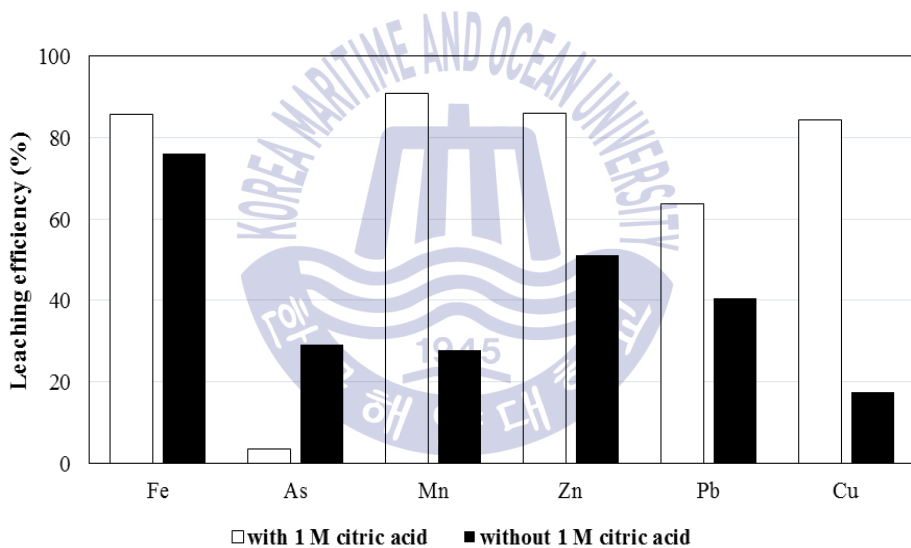


Fig. 4.4 Effect of addition of citric acid on the leaching efficiency of metals in 1.0 M Fe^{3+} , 50 °C, 400 rpm, 0.25 % pulp density, and 3 h leaching time.

4.2.2. Effect of citric acid addition

It was found that metal extraction could reach the equilibrium with 3.0 M ferric concentration in 3 h of leaching test. In fact, however, the acidity of concentrated ferric chloride due to the hydrolysis processes could affect to the soil after treatment. Therefore, to reduce this problem, 1.0 M Fe^{3+} was chosen to investigate the effect of citric acid addition.

To ascertain the effect of citric acid on the metal extraction, it is necessary to investigate the presence and absence of citric acid, along with ferric chloride media. The leaching was conducted under the conditions of temperature 50 °C, agitation speed 400 rpm, leaching time 3 h, Fe^{3+} concentration 1.0 M, and pulp density 0.25 %. Comparisons between the percentages of heavy metals removal using 1.0 M Fe^{3+} with 1.0 M citric acid and 1.0 M Fe^{3+} without citric acid showed that the addition of citric acid enhanced the leaching efficiencies of metals. Leaching efficiencies increased 76.2 – 85.8 %, 27.7 – 90.9 %, 51.1 – 86.1 %, 40.6 – 63.8 %, and 17.5 – 84.4 % for Fe, Mn, Zn, Pb, and Cu, respectively. However in the case of As, the addition of citric acid reduced the leaching efficiency from 29.2 % to 3.5 %. These results indicated that synergetic effect was obtained by using both Fe^{3+} and citric acid, which could be supported by ORP (Oxidation-Reduction Potential) value of solution. Without citric acid in solution, ORP value was 713.5 mV (vs Ag/AgCl), whereas it was 656.1 mV (vs Ag/AgCl) with 1.0 M citric acid and 1.0 M Fe^{3+} concentration, respectively. On the other hand, Ji and his coworkers (2007) reported that citric acid could play as a role of the reductant for Au and Ag reduction led to reduce the effect of ferric chloride in solution.

4.2.3. Effect of pH

In further exploration, the acidity of the solution was varied. As well known, pH solution is an important parameter to the efficiency of heavy metal extraction from soil. Under the conditions of 1.0 M Fe^{3+} with adjusting the ratio of citric acid and sodium nitrate, the effect

of pH solution (0, 1.0, 1.5, and 2.0) was performed to investigate the leaching behavior of metals.

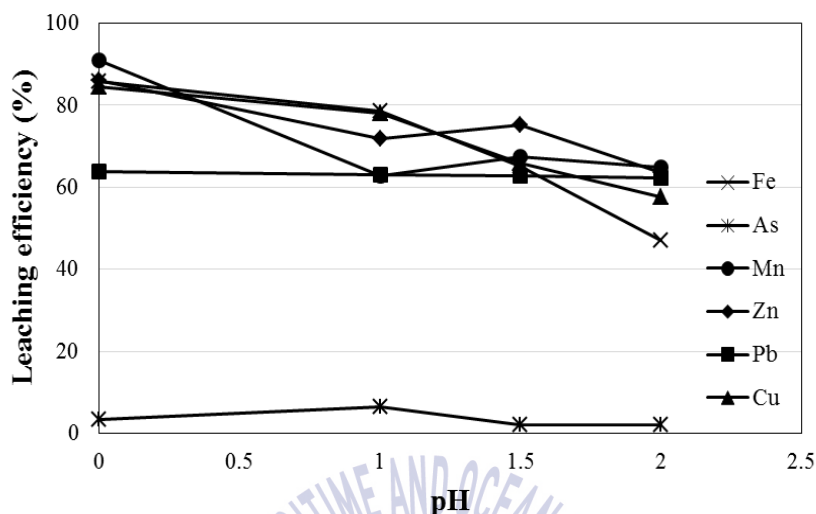


Fig. 4.5 Effect of addition of pH on the leaching behavior of metals in 1.0 M Fe³⁺, 50 °C, 400 rpm, 0.25 % pulp density, and 3 h leaching time.

The leaching of all metals gradually decreased with increasing pH value from 0 to 2.0 as shown in Figure 4.5, which illustrated that the increase in acidity might be expected to increase the leaching efficiencies. The reduced efficiencies of metals at pH 0-2 can be observed with Fe 85.8 – 47.1 %, Mn 90.9 – 64.8 %, Zn 86.1 – 63.4 %, Pb 63.8 – 62.2 %, and Cu 84.4 – 57.6 %. This data showed that Pb was the most independent of pH change (1.4 %) and Fe was the most sensitive to the pH change (38.8 %). On the other hand, the extraction of metals had the same trend from pH 1.0 to pH 1.5. Therefore, with the aim at reducing the acidity of solution, pH 1.5 was chosen as the optimum pH value, respectively.

4.2.4. Effect of temperature

The effect of temperature (30 – 90 °C) was investigated in 1.0 M Fe³⁺, at 400 rpm, 3 h leaching time, 0.25 % pulp density, and pH 1.5.

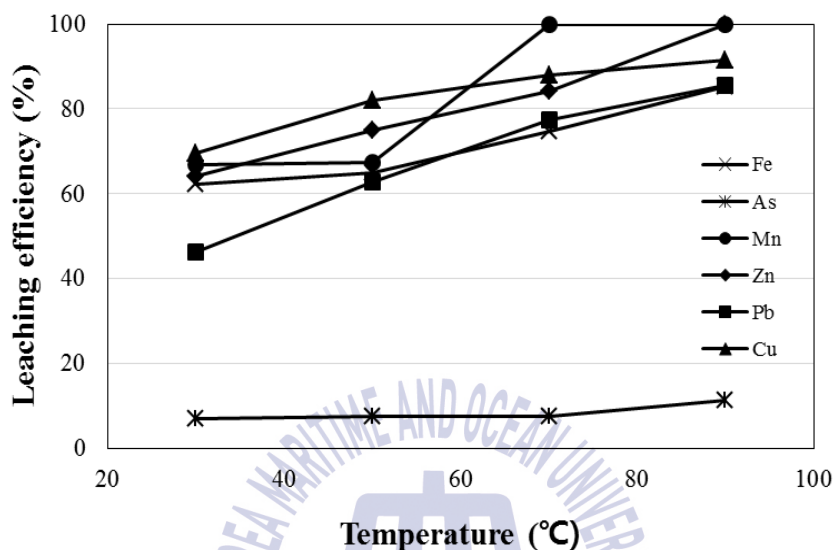


Fig. 4.6 Effect of temperature on the leaching behavior of metals in 1.0 M Fe³⁺, 400 rpm, 0.25 % pulp density, pH 1.5, and 3 h leaching time.

Figure 4.6 showed the significant increase of leaching behavior of metals as temperature from 30 °C to 90 °C. On the other hand, the positive effect of temperature on metal extraction with ferric chloride solution was also reported in several studies (Al-Harashsheh et al., 2008; Aydogan et al., 2005). The effect was found to be the maximum at 90 °C with 100 % of total Mn and Zn concentration were extracted in solution, higher than 85 % extracted efficiencies of other metals were also observed with Fe 85.2 %, Pb 85.5 %, and Cu 91.6 %, respectively. The data, however, showed that As leaching efficiency just increased from 7.1 % to 11.2 % with the increase of temperature from 30 °C to 90 °C. The temperature presented an important role in metal dissolution process when enhancing extraction efficiency significantly. Hence, 90 °C of solution temperature was selected to

investigate the effect of agitation speed on leaching behavior.

4.2.5. Effect of agitation speed

The effect of agitation speed on leaching behavior of metals was examined to identify the rate controlling step. The leaching tests were performed in the range of 200 – 600 rpm to investigate the effect of liquid film boundary diffusion surrounding solid particles on leaching efficiency of metals in 1.0 M Fe³⁺ at 90 °C temperature, with 3 h leaching time, 0.25 % pulp density, and pH 1.5. The leaching efficiencies increased gradually from 200 rpm to 400 rpm. The percentages of Fe, Mn, Zn, Pb, and Cu increased from 72 – 85.2 %, 96 – 100 %, 92 – 100 %, 58.2 – 85.5 %, and 70.7 – 91.6 %. The leaching efficiencies then remained almost constant from 400 rpm until 600 rpm. Hence, to ensure the effect of particle suspension in the solution, an operating agitation speed of 400 rpm was selected in subsequent leaching tests.

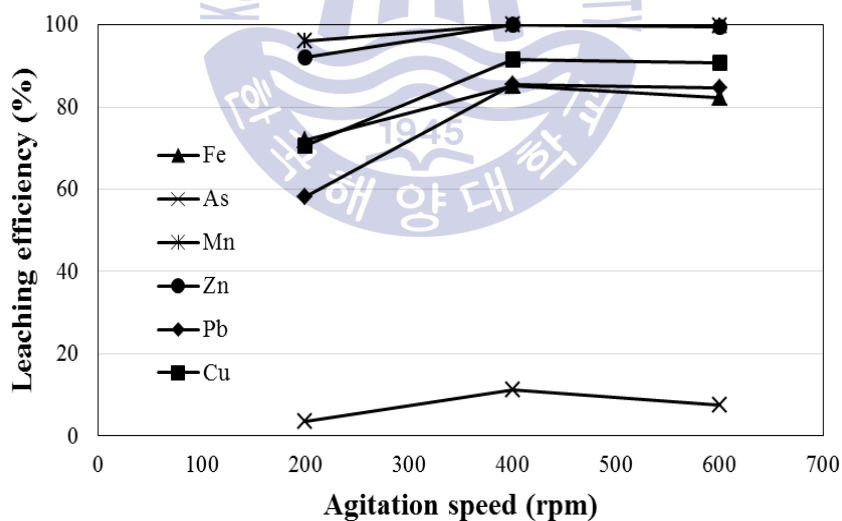


Fig. 4.7 Effect of agitation speed on the leaching behavior of metals in 1.0 M Fe³⁺ 90 °C, 0.25 % pulp density, pH 1.5, and 3 h leaching time.

4.2.6. Effect of pulp density

Finally, to further investigate the parameters could affect the metal extraction by leaching, the effect of pulp density was conducted to evaluate and optimize the consumption of leaching reagents for the effective removal of heavy metals.

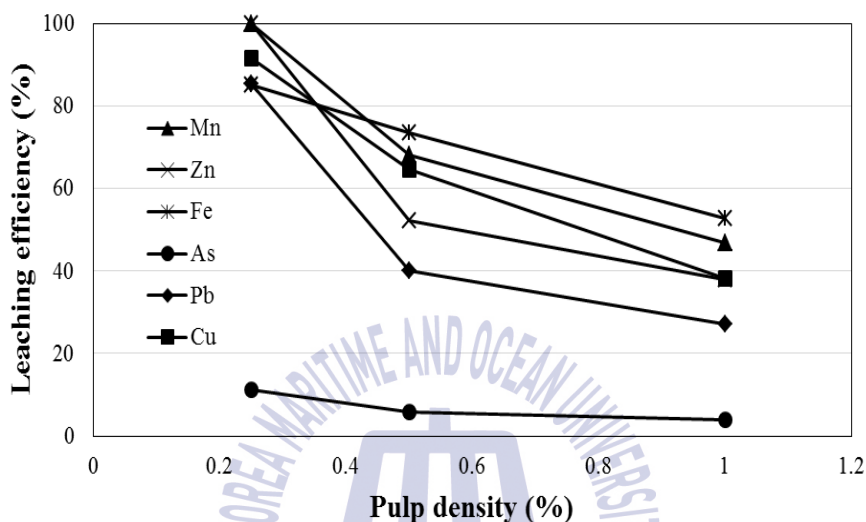


Fig. 4.8 Effect of pulp density on the leaching behavior of metals in 1.0 M Fe^{3+} , 90 °C, 400 rpm, pH 1.5, and 3 h leaching time.

In fact, figure 4.8 showed the effect of pulp density on the leaching behavior of metals in the range from 0.25 % to 1.0 % at 1.0 M Fe^{3+} , 90 °C of solution temperature at the controlled agitation speed 400 rpm, pH 1.5, and in 3 h leaching time. As can be seen, the leaching efficiencies drastically decreased with increasing pulp density. From 0.25 – 1.0 % of pulp density, the percentages of metal extraction decreased with Fe 85.2 – 52.6 %, As 11.2 – 4.0 %, Mn 100 – 46.8 %, Zn 100 – 37.9 %, Pb 85.5 – 27.1 %, and Cu 91.6 – 38.1 %. Due to the high content of metals in mine tailings, the leaching tests were performed with low pulp density to observe the leaching behavior of metals exactly as well as to yield high leaching efficiency. Therefore, 0.25 % of pulp density was selected as the optimum condition.

4.3. Low leaching efficiency of As investigation

A number of researchers have studied about the remediation of As from the tailing and contaminated soil in several methods (Oniret & Lin, 2016; Jang et al., 2005). It was found that the tailing tends to have low pH value might be caused by producing sulfide minerals such as arsenopyrite (FeAsS) and pyrite (FeS₂) (Dold, 2000). Moreover, As in soils tends to be bound to iron compounds through iron arsenate/arsenite or adsorption to iron oxides/hydroxides (Goldberg & Johnston, 2001; Bowell, 1994). On the other hand, it can be observed that the extracted As in the tailings by using 0.05 – 0.1 M citric acid obtained only 5 – 10 % total As concentration in 24 hours (Jang et al., 2005). Recalling this study results, the same tendency was also observed (only 3.5 % As was extracted) when using 1.0 M citric acid combined with 1.0 M Fe³⁺. Furthermore, the highest extracted As in this study was only 11.2 % under the conditions of 1.0 M Fe³⁺, pH 1.5, 90 °C of solution temperature and after 3 h of leaching test. Hence, the low leaching efficiency of As was carried out to investigate such as ORP solution values, rest potential, and XRD pattern observation.

4.3.1. ORP solution values

The enhancement of metal extraction by ferric chloride was affected by various types of chelating agent, probably due to the different Oxidation Reduction Potential (ORP) of an agent when combining chemical reagents. Therefore, the differences of the ORP values between with and without citric acid in ferric chloride solution media were assumed to affect to leaching efficiencies. While the ORP of 1.0 M Fe³⁺ solution was measured up to 713.5 mV (vs Ag/AgCl), on the other hand, the ORP of 1.0 M Fe³⁺ combining with 1.0 M citric acid reduced to 656.1 mV (vs Ag/AgCl). This reducing potential led to low leaching efficiency of As in solution.

4.3.2. XRD pattern observation

The initial sample and the residue after leaching were subjected to XRD analysis to observe the phase changes. Figure 3.1 and Figure 4.9 showed the changing XRD analysis between the initial sample and the residue after leaching using 1.0 M Fe^{3+} , pH 1.5 at 90 °C, 400 rpm, and pulp density 0.25 %. It was found that the detected components after leaching included SiO_2 , As_2O_3 , and FeAsS , which contained As in both initial sample and residue after leaching. Results, therefore, showed the good agreement between the XRD analysis and leaching efficiencies due to the significant remaining of As in the leached residue.

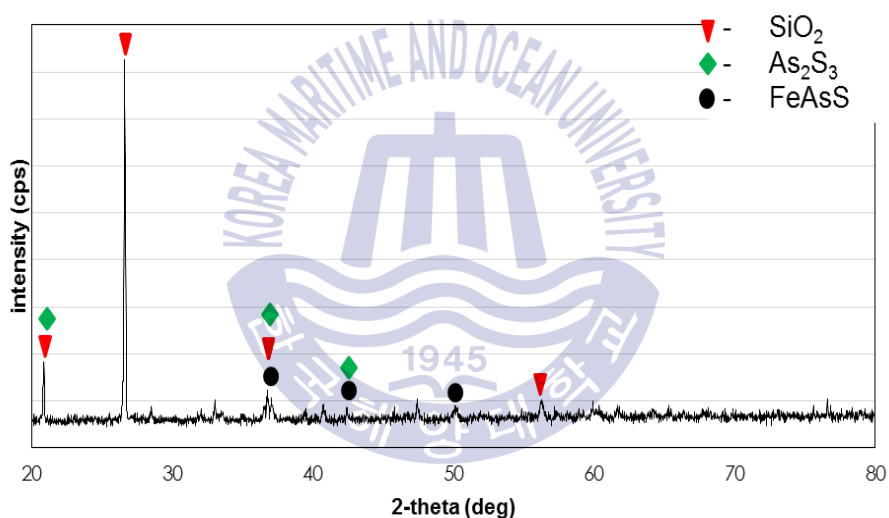


Fig. 4.9 X-ray diffraction pattern of residue sample after leaching with 1.0 M Fe^{3+} , pH 1.5, 90 °C temperature, 400 rpm, and 0.25 % of pulp density.

4.3.3. Rest potential value

To investigate the low leaching rate of arsenic sulfide minerals, rest potential of sulfide minerals with different types of collectors were also carried out. Table 4.1 presented the rest potential of several sulfide minerals with potassium ethyl xanthate.

Table 4.1 Products of the interaction of sulfide minerals with potassium ethyl xanthate and measured rest potential. Potassium ethyl xanthate (6.25×10^{-4} mol/L at pH = 7) reversible potential for oxidation to dixanthogen is 0.13 V (Yuehua et al., 2009).

Minerals	Rest potential (V)
pyrite	0.22
arsenopyrite	0.22
pyrrhotite	0.21
molybdenite	0.16
chalcopyrite	0.14
alabandite	0.15
covellite	0.05
borinite	0.06
galena	0.06

It was agreed that the rest potential provide the information to determine the reactions that take place at the mineral surface and the rates of these processes. This table illustrated that pyrite and arsenopyrite showed the highest rest potential value. This result concluded, hence, metal extraction of the mine tailing was hindered by sulfide mineral compounds.

Chapter 5 Conclusion

In this present study, the sequential extraction and leaching tests for contaminated soil containing As and other heavy metals such as Fe, Mn, Zn, Cu, and Pb were carried out to investigate the leaching behavior by using citric acid and ferric chloride combination.

In the sequential extraction tests, the individual metal fraction did not correlate between the 1.0 g sample result and 0.2 g sample result. In 1.0 g soil sample followed Tessier's procedure, metal proportions observed in the residual fraction were 85.46 %, 97.7 %, 25.82 %, 68.76 %, 55.43 %, and 68.23 % for Fe, As, Mn, Zn, Pb, and Cu. On the other hand, with 0.2 g sample, it changed to 57.36 % Fe, 71.43 % As, 2.20 % Mn, 25.02 % Zn, 51.79 % Pb, and 29.87 % Cu, respectively. Recalling the diversity of existing procedures in sequential extraction, the differences could be explained due to the high content of metals in tailing samples, the use of reagents with less amount of sample is more sufficient to extract the individual metal species from soil surface completely. It was, therefore, demonstrated that the use of 0.2 g sample in this study would obtain more exact information about metal speciation, and then the further suitable evaluation could be carried out.

The leaching behaviors of heavy metals from tailings, which have caused the soil contamination near abandoned mine sites, were investigated using citrate solution with ferric ion. The combination of citrate and ferric chloride enhanced the leaching efficiencies of heavy metals except As, which could be achieved by complexing and oxidizing powers of citrate and ferric ion, respectively. However, the addition of citrate partially reduced the oxidizing power and limited the dissolution of As in solution. The results, on the other hand, indicated that As could be separated selectively in the residue by the combination of citrate and ferric ion. Therefore, this method can be applied for treating As separately from other heavy metals from this mine tailings.

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