Remediation of Heavy Metals:
in the area Gangneung-si Okgye-myeon
(강릉시 옥계면) Industrial Complex

Imasha Pasqual

2010-12129

Table of contents

1. Introduction

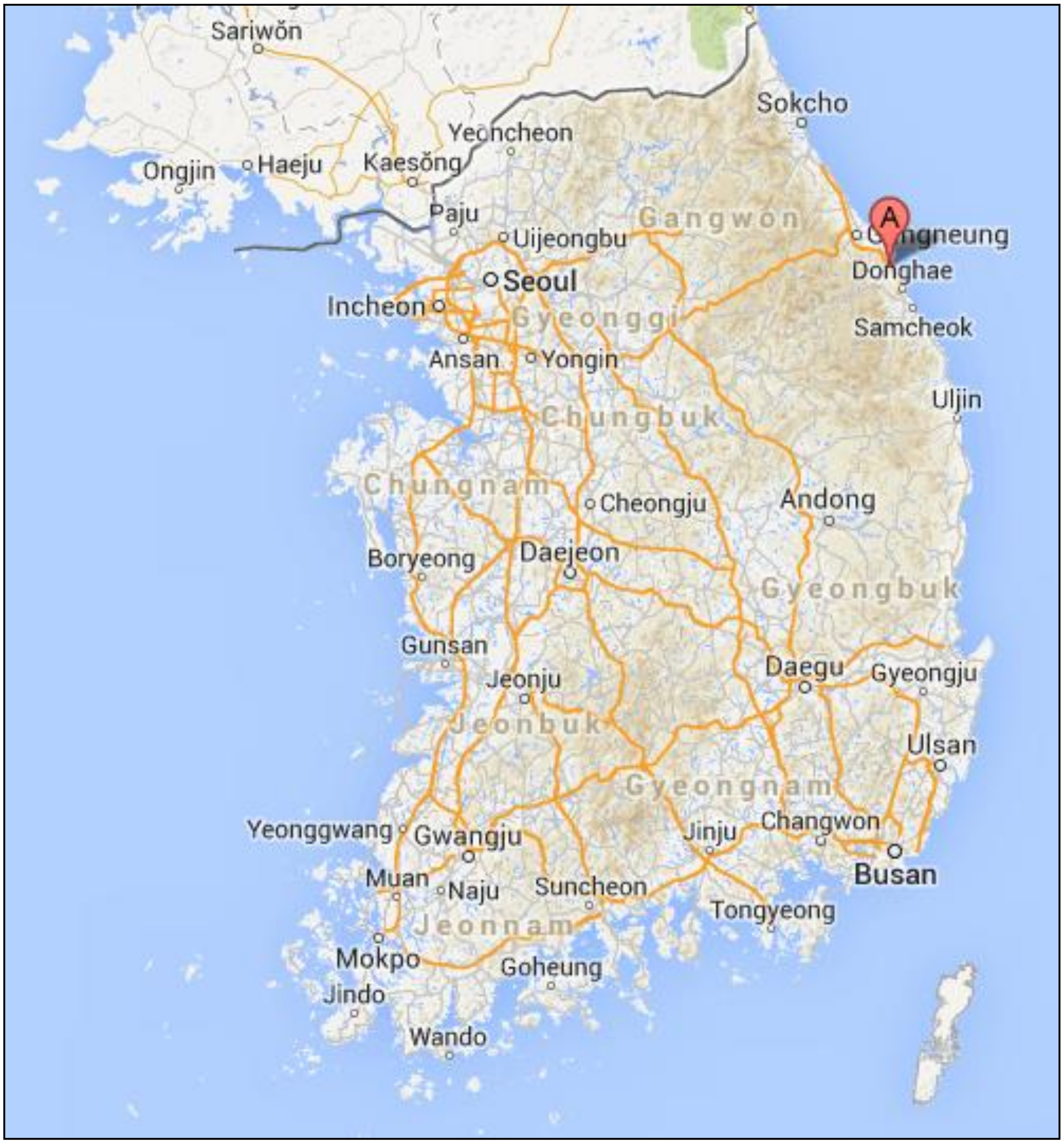


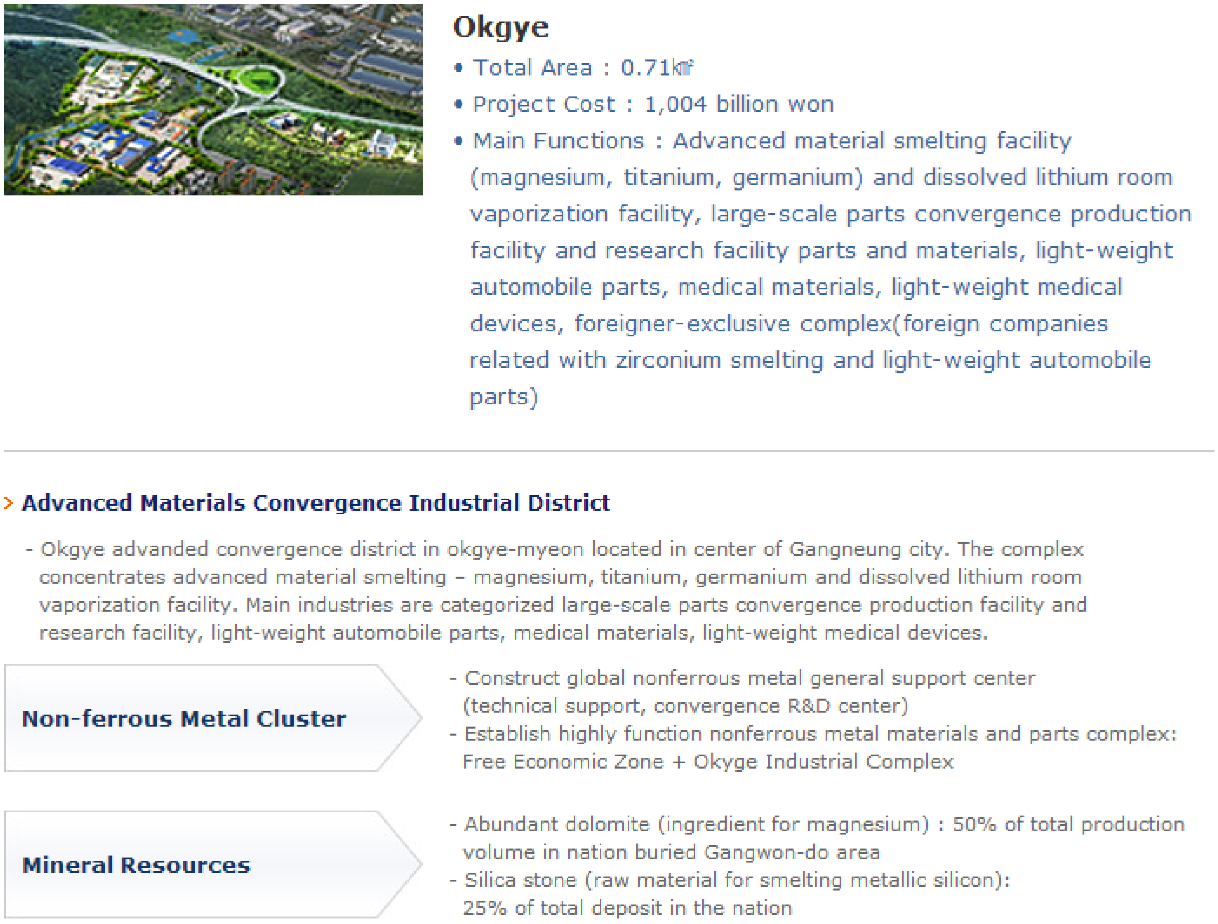
Figure 1: Location of Okgye-myeon in South Korea(as marked in red A pin)

Remediation of heavy metals found in the soil from the area Okgye-myeon in South Korea (as given in Figure 1 above) was considered in this study. This introduction consists of relevant information of the area, heavy metals and remediation methods.

1.1. Soil Survey of Area

Figure 2: Area considered in this study (marked in red)

Okgye-myeon (옥계면) is at the south end of Gangneung-shi, closer to Donghae. The specific area considered in this study is marked in red in the figure 2 above. As it can be seen in the satellite image this area is near to the beach consisting both of over thousand residences and also of plain empty land. The area is approximately 40,000 m^2 and is also near few industrial facilities. More information about the industrialization of this area is given in figure 3 below. The geological characteristics of the area considered are given in the Table 1.



Okgye

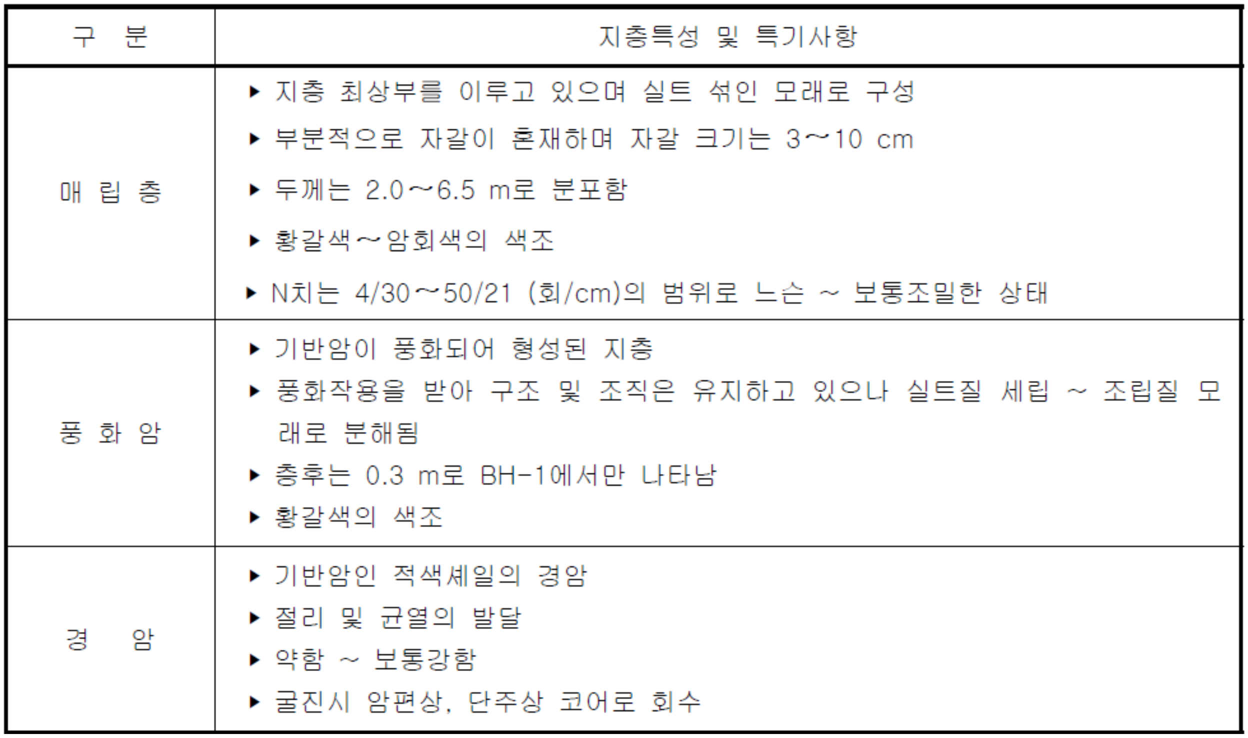
- Total Area : 0.71㎢
- Project Cost : 1,004 billion won
- Main Functions : Advanced material smelting facility (magnesium, titanium, germanium) and dissolved lithium room vaporization facility, large-scale parts convergence production facility and research facility parts and materials, light-weight automobile parts, medical materials, light-weight medical devices, foreigner-exclusive complex(foreign companies related with zirconium smelting and light-weight automobile parts)

› Advanced Materials Convergence Industrial District

- Okgye advanded convergence district in okgye-myeon located in center of Gangneung city. The complex concentrates advanced material smelting – magnesium, titanium, germanium and dissolved lithium room vaporization facility. Main industries are categorized large-scale parts convergence production facility and research facility, light-weight automobile parts, medical materials, light-weight medical devices.

Non-ferrous Metal Cluster	- Construct global nonferrous metal general support center (technical support, convergence R&D center) - Establish highly function nonferrous metal materials and parts complex: Free Economic Zone + Okyge Industrial Complex
Mineral Resources	- Abundant dolomite (ingredient for magnesium) : 50% of total production volume in nation buried Gangwon-do area - Silica stone (raw material for smelting metallic silicon): 25% of total deposit in the nation

Figure 3: Information of Industrialization of Okgye



구 분	지층특성 및 특기사항
매 립 층	▸ 지층 최상부를 이루고 있으며 실트 섞인 모래로 구성 ▸ 부분적으로 자갈이 혼재하며 자갈 크기는 3~10 cm ▸ 두께는 2.0~6.5 m로 분포함 ▸ 황갈색~암회색의 색조 ▸ N치는 4/30~50/21 (회/cm)의 범위로 느슨 ~ 보통조밀한 상태
풍 화 암	▸ 기반암이 풍화되어 형성된 지층 ▸ 풍화작용을 받아 구조 및 조직은 유지하고 있으나 실트질 세립 ~ 조립질 모래로 분해됨 ▸ 층후는 0.3 m로 BH-1에서만 나타남 ▸ 황갈색의 색조
경 암	▸ 기반암인 적색셰일의 경암 ▸ 절리 및 균열의 발달 ▸ 약함 ~ 보통강함 ▸ 굴진시 암편상, 단주상 코어로 회수

Table 1: Geological characteristics of the considered area

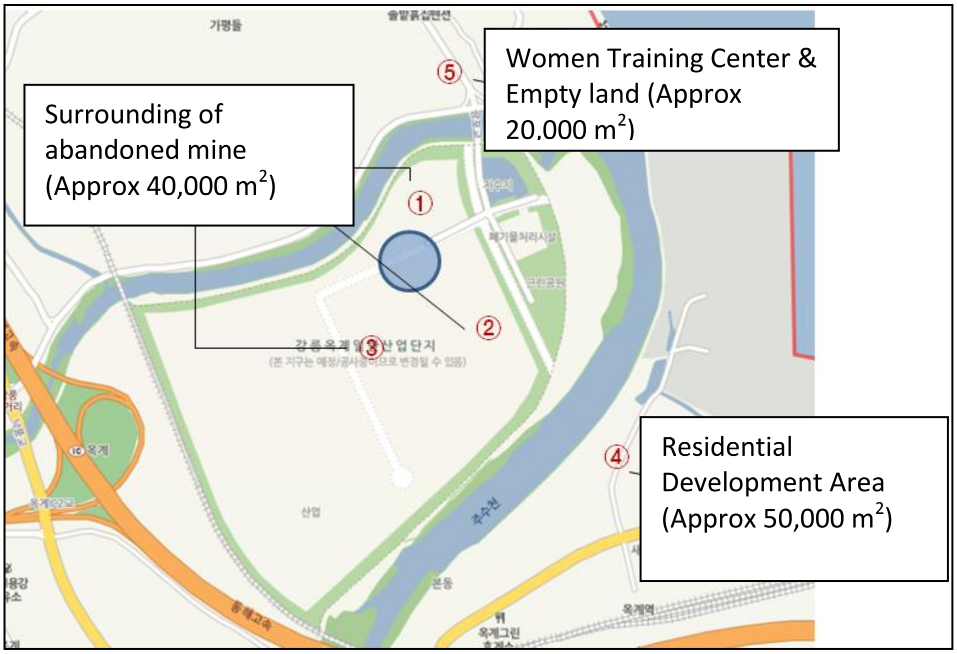
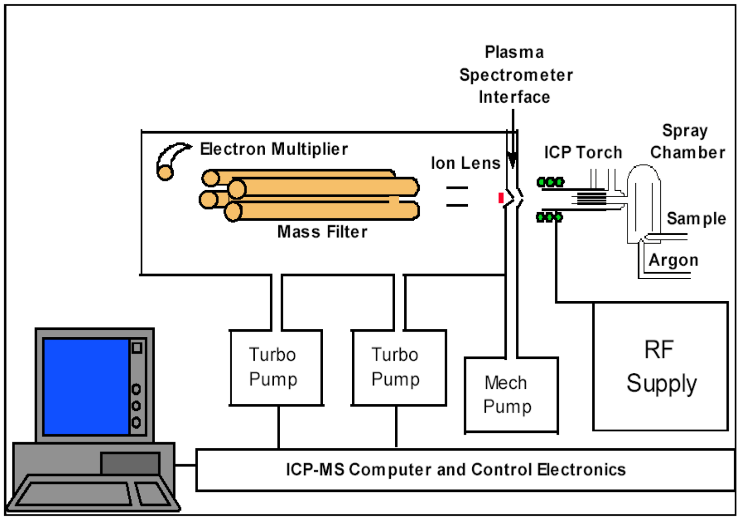


Figure 4: Division of considered area for analysis

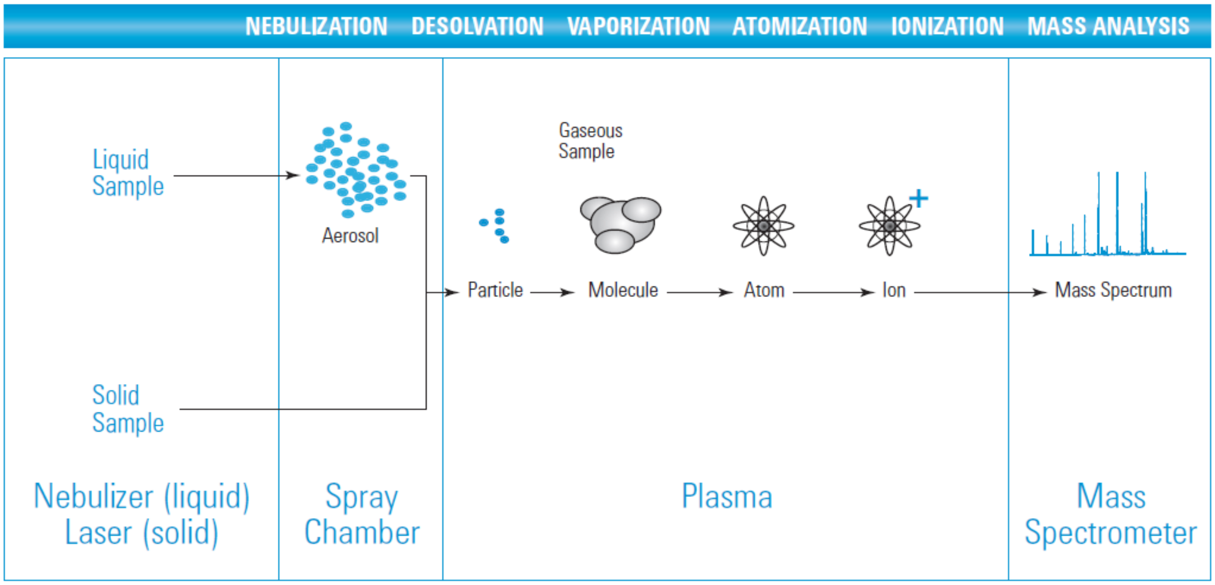
In this study we consider soil survey of five sections of land with different characteristics in three general directions as shown in figure 4 above.

Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) was carried out to detect metals in the samples of soil. This is achieved by ionizing the sample with inductively coupled plasma and then using a mass spectrometer to separate and quantify those ions.

a) ICP-MS instrument



b) Components of the instrument



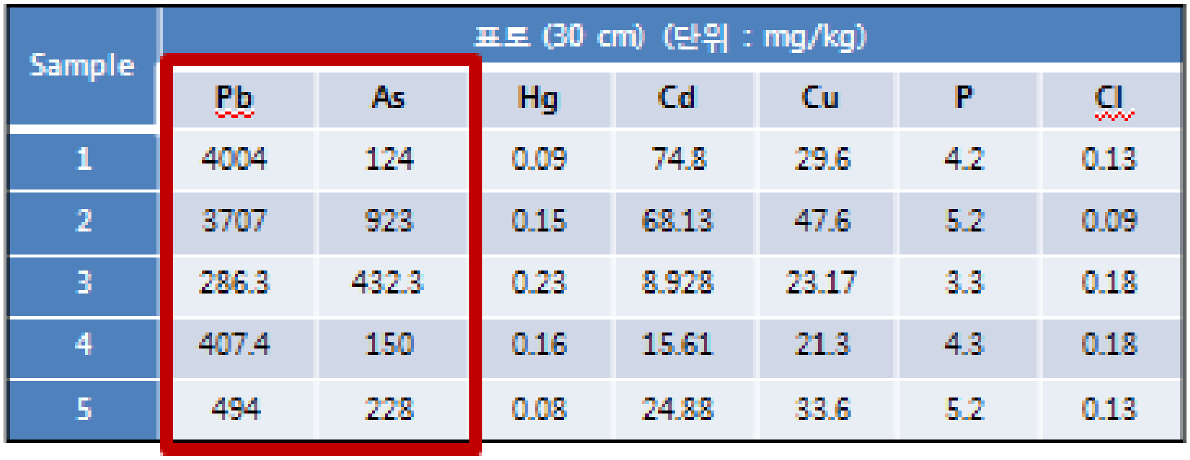
c) Brief process of ICP-MS

Figure 5: Inductively Coupled Plasma-Mass Spectroscopy

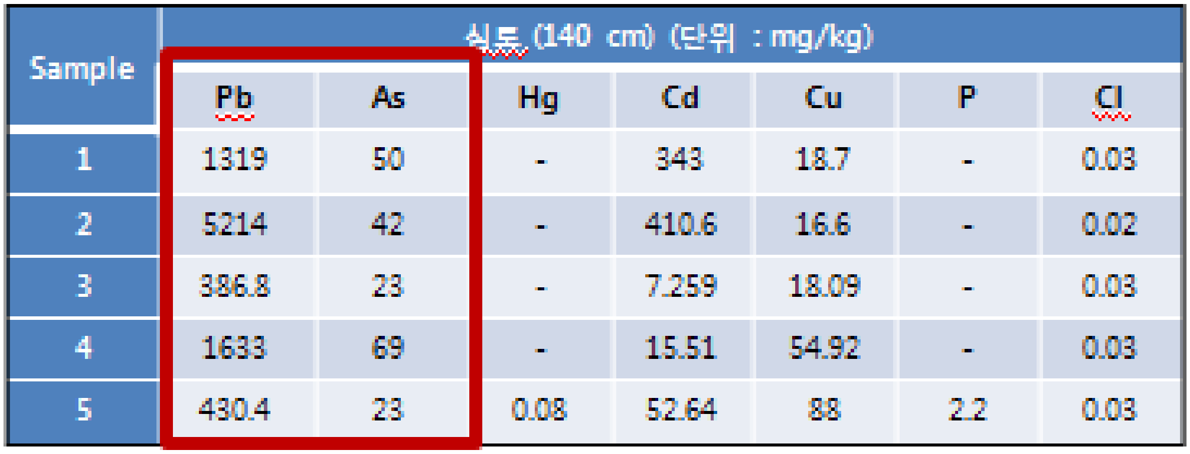
1.2. Heavy Metals present in the area

The soil samples taken from the five sections of land gave following results for surface soil and subsoil:

Table 2: Heavy metals present in Soil a) surface soil b) subsoil



Sample	표토 (30 cm) (단위 : mg/kg)						
	Pb	As	Hg	Cd	Cu	P	Cl
1	4004	124	0.09	74.8	29.6	4.2	0.13
2	3707	923	0.15	68.13	47.6	5.2	0.09
3	286.3	432.3	0.23	8.928	23.17	3.3	0.18
4	407.4	150	0.16	15.61	21.3	4.3	0.18
5	494	228	0.08	24.88	33.6	5.2	0.13



Sample	심토 (140 cm) (단위 : mg/kg)						
	Pb	As	Hg	Cd	Cu	P	Cl
1	1319	50	-	343	18.7	-	0.03
2	5214	42	-	410.6	16.6	-	0.02
3	386.8	23	-	7.259	18.09	-	0.03
4	1633	69	-	15.51	54.92	-	0.03
5	430.4	23	0.08	52.64	88	2.2	0.03

It can be seen that from the total percentage of heavy metal present in soil 33% is Lead (Hereafter referred to as Pb) and 60% is Arsenic (hereafter referred to as As). Therefore it can be concluded that there is a serious issue of Pb pollution in overall soil and As pollution in surface soil.

Therefore let us study about Arsenic and Lead in more detail.

1.2.1. Arsenic

Human activity is responsible for 80.000 tons of Arsenic per year released by the burning of fossil fuels. Arsenic is a component that is extremely hard to convert to water-soluble or volatile products. The fact that arsenic is naturally a fairly a mobile component means that large concentrations are not likely to appear on one specific site. However the negative side to it is that arsenic pollution becomes a wider issue because it easily spreads. Arsenic cannot be mobilized easily when it is immobile. Due to human activities, mainly through mining and melting, naturally immobile arsenics have also mobilized and can now be found on many more places than where they existed naturally. Most Arsenic is found in conjunction with sulfur in minerals such as arsenopyrite (AsFeS), realgar, orpiment and enargite. Non is mined as such because it is produced as a by-product of refining the ores of other metals, such as copper and lead. World production of arsenic, in the form of its oxide, is around 50.000 tons per year, far in excess of that required by industry. World resources of arsenic in copper and lead ores exceed 10 million tons.

Health effects of arsenic

Arsenic is one of the most toxic elements that can be found. Despite their toxic effect, inorganic arsenic bonds occur on earth naturally in small amounts. Humans may be exposed to arsenic through food, water and air. Exposure may also occur through skin contact with soil or water that contains arsenic. Levels of arsenic in food are fairly low, as it is not added due to its toxicity. But levels of arsenic in fish and seafood may be high, because fish absorb arsenic from the water they live in. Luckily this is mainly the fairly harmless organic form of arsenic, but fish that contain significant amounts of inorganic arsenic may be a danger to human health. Arsenic exposure may be higher for people that work with arsenic, for people that live in houses that contain conserved wood of any kind and for those who live on farmlands where arsenic-containing pesticides have been applied in the past.

Exposure to inorganic arsenic can cause various health effects, such as irritation of the stomach and intestines, decreased production of red and white blood cells, skin changes and lung irritation. It is suggested that the uptake of significant amounts of inorganic arsenic can intensify the chances of cancer development, especially the chances of development of skin cancer, lung cancer, liver cancer and lymphatic cancer. A very high exposure to inorganic arsenic can cause infertility and miscarriages with women, and it can cause skin disturbances, declined resistance to infections, heart disruptions and brain damage with both men and women. Finally, inorganic arsenic can damage DNA. A lethal dose of arsenic oxide is generally regarded as 100 mg. Organic Arsenic can cause neither cancer, nor DNA damage. But exposure to high doses may cause certain effects to human health, such as nerve injury and stomachaches.

Environmental effects of arsenic

The arsenic cycle has broadened as a consequence of human interference and due to this, large amounts of arsenic end up in the environment and in living organisms. Arsenic is mainly emitted by the copper producing industries, but also during lead and zinc production and in agriculture. It cannot be destroyed once it has entered the environment, so that the amounts that we add can spread and cause health effects to humans and animals on many locations on earth.

Plants absorb arsenic fairly easily, so that high-ranking concentrations may be present in food. The concentrations of the dangerous inorganic arsenics that are currently present in surface waters enhance the chances of alteration of genetic materials of fish. This is mainly caused by accumulation of arsenic in the bodies of plant-eating freshwater organisms. Birds eat the fish that already contain eminent amounts of arsenic and will die as a result of arsenic poisoning as the fish is decomposed in their bodies.

1.2.2. Lead

Native lead is rare in nature. Currently lead is usually found in ore with zinc, silver and copper and it is extracted together with these metals. The main lead mineral in Galena (PbS) and there are also deposits of cerrussite and anglesite which are mined. World production of new lead is 6 million tons a year, and workable reserves total are estimated 85 million tons, which is less than 15 year's supply.

Lead occurs naturally in the environment. However, most lead concentrations that are found in the environment are a result of human activities. Due to the application of lead in gasoline an unnatural lead-cycle has consisted. In car engines lead is burned, so that lead salts (chlorines, bromines, oxides) will originate. These lead salts enter the environment through the exhausts of cars. The larger particles will drop to the ground immediately and pollute soils or surface waters, the smaller particles will travel long distances through air and remain in the atmosphere. Part of this lead will fall back on earth when it is raining. This lead-cycle caused by human production is much more extended than the natural lead-cycle. It has caused lead pollution to be a worldwide issue.

Health effects of lead

Lead is a soft metal that has known many applications over the years. It has been used widely since 5000 BC for application in metal products, cables and pipelines, but also in paints and pesticides. Lead is one out of four metals that have the most damaging effects on human health. It can enter the human body through uptake of food (65%), water (20%) and air (15%). Foods such as fruit, vegetables, meats, grains, seafood, soft drinks and wine may contain significant amounts of lead. Cigarette smoke also contains small amounts of lead. Lead can enter (drinking) water through corrosion of pipes. This is more likely to happen when the water is slightly acidic. That is why public water treatment systems are now required to carry out pH-adjustments in water that will serve drinking purposes. For as far as we know, lead fulfils no essential function in the human body, it can merely do harm after uptake from food, air or water.

Lead can cause several unwanted effects, such as:

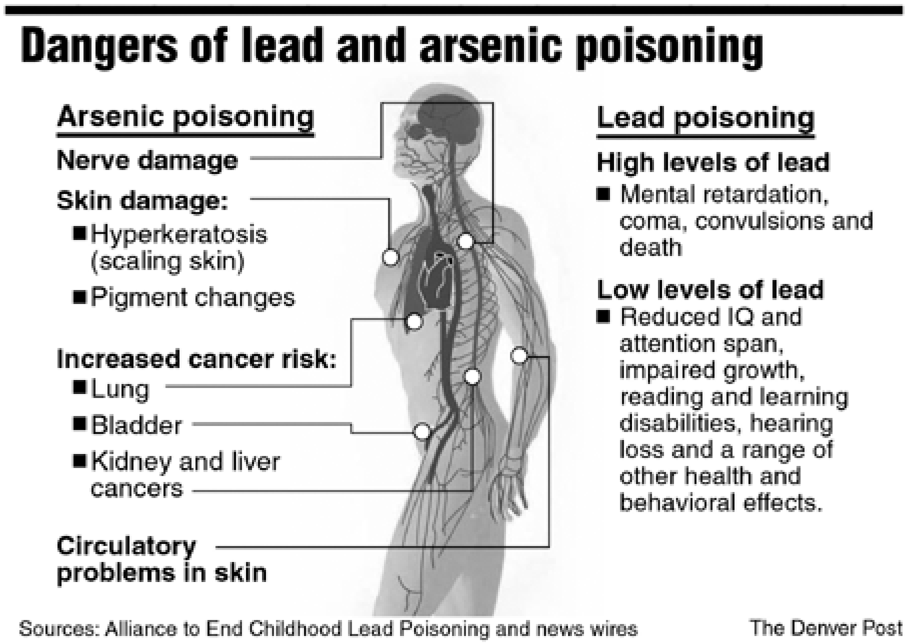
- Disruption of the biosynthesis of hemoglobin and anemia
- A rise in blood pressure
- Kidney damage
- Miscarriages and subtle abortions
- Disruption of nervous systems
- Brain damage
- Declined fertility of men through sperm damage

- Diminished learning abilities of children
- Behavioral disruptions of children, such as aggression, impulsive behavior and hyperactivity

Lead can enter a fetus through the placenta of the mother. Because of this it can cause serious damage to the nervous system and the brains of unborn children.

Environmental effects of lead

Not only leaded gasoline causes lead concentrations in the environment to rise. Other human activities, such as fuel combustion, industrial processes and solid waste combustion, also contribute. Lead can end up in water and soils through corrosion of leaded pipelines in a water transporting system and through corrosion of leaded paints. It cannot be broken down; it can only convert to other forms. Lead accumulates in the bodies of water organisms and soil organisms. These will experience health effects from lead poisoning. Health effects on shellfish can take place even when only very small concentrations of lead are present. Body functions of phytoplankton can be disturbed when lead interferes. Phytoplankton is an important source of oxygen production in seas and many larger sea-animals eat it. Soil functions are disturbed by lead intervention, especially near highways and farmlands, where extreme concentrations may be present. Soil organisms than suffer from lead poisoning, too.
Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains.



Sources: Alliance to End Childhood Lead Poisoning and news wires The Denver Post

Figure 6: Health effects of Lead and Arsenic

It can be concluded that as shown in Figure 6 above increased amounts of Lead and Arsenic can be a serious issue for health.

1.2.3. Conclusion on Heavy metal pollution

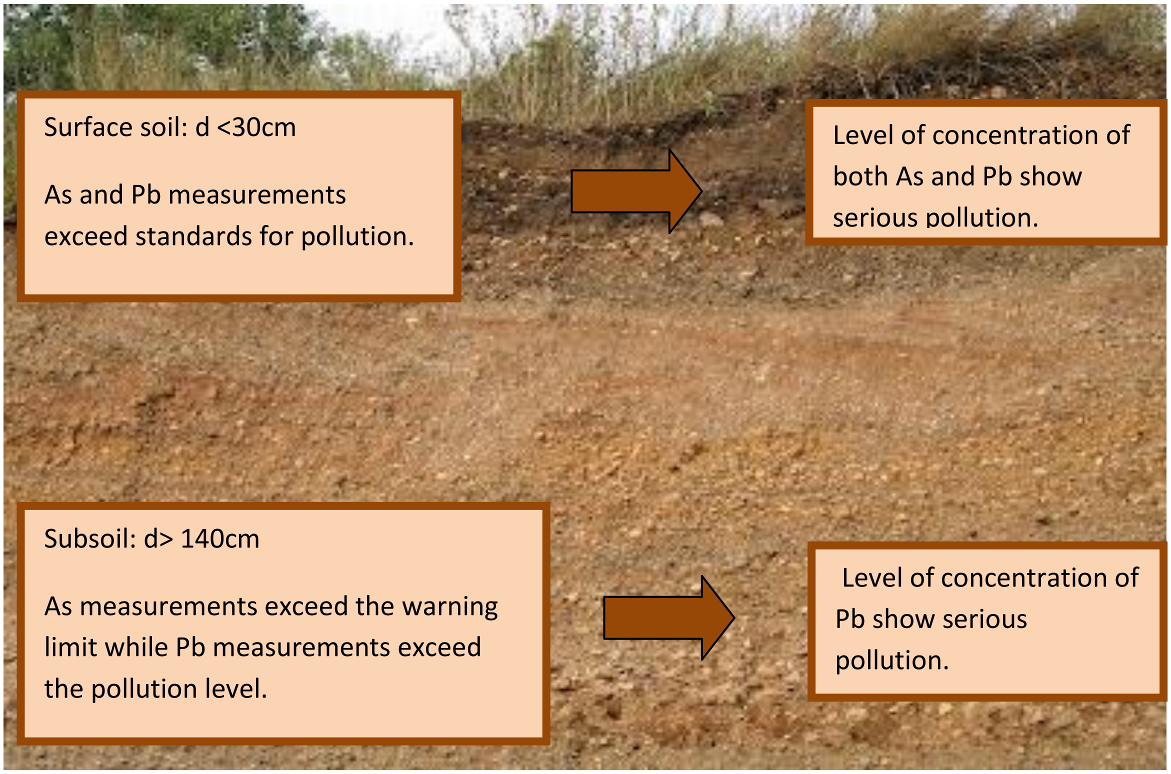
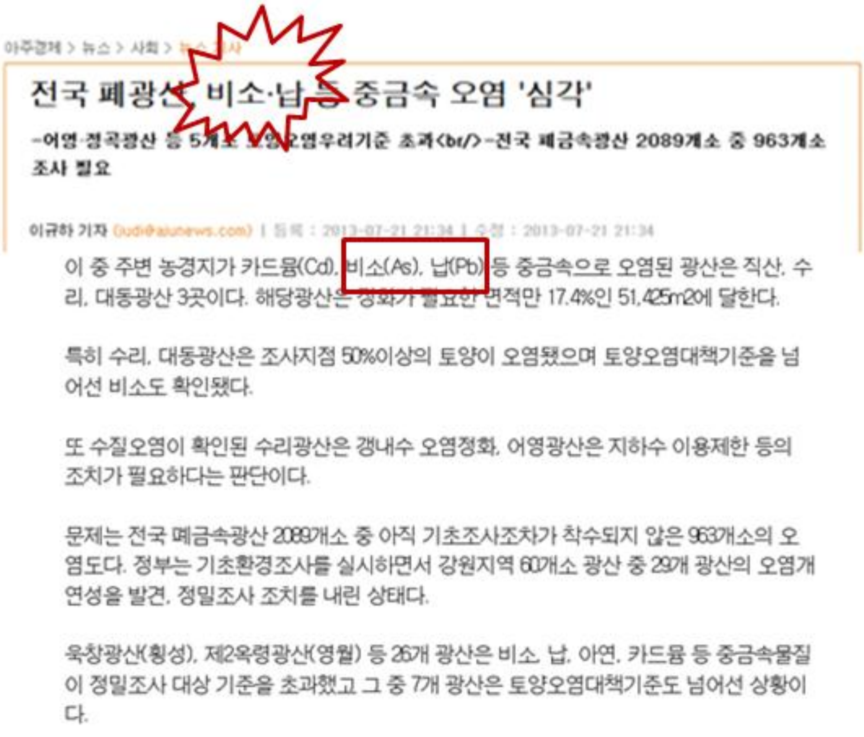


Figure 7: Conclusion from analysis of soil


아주경제 > 뉴스 > 사회 > 뉴스기사

전국 폐광산 비소·납 등 중금속 오염 '심각'

-어영·정곡광산 등 5개소 토양오염우려기준 초과
-전국 폐금속광산 2089개소 중 963개소 조사 필요

이규하 기자 (judi@ajunews.com) | 등록 : 2013-07-21 21:34 | 수정 : 2013-07-21 21:34

이 중 주변 농경지가 카드뮴(Cd), 비소(As), 납(Pb) 등 중금속으로 오염된 광산은 직산, 수리, 대동광산 3곳이다. 해당광산은 정화가 필요한 면적만 17.4%인 51,425m2에 달한다.

특히 수리, 대동광산은 조사지점 50%이상의 토양이 오염됐으며 토양오염대책기준을 넘어선 비소도 확인됐다.

또 수질오염이 확인된 수리광산은 갱내수 오염정화, 어영광산은 지하수 이용제한 등의 조치가 필요하다는 판단이다.

문제는 전국 폐금속광산 2089개소 중 아직 기초조사조차가 착수되지 않은 963개소의 오염도다. 정부는 기초환경조사를 실시하면서 강원지역 60개소 광산 중 29개 광산의 오염개연성을 발견, 정밀조사 조치를 내린 상태다.

욱창광산(횡성), 제2옥령광산(영월) 등 26개 광산은 비소, 납, 아연, 카드뮴 등 중금속물질이 정밀조사 대상 기준을 초과했고 그 중 7개 광산은 토양오염대책기준도 넘어선 상황이다.

http://www.ajunews.com/kor/view.jsp?newsId=20130721000036

Figure 8: News article on As & Pb pollution

The graphical conclusion from the analysis of soil samples is shown in the figure 7 above. Furthermore the news article given in Figure 8 show how Pb and As has become a serious issue of soil pollution. Therefore it is important to employ remediation methods as soon as possible.

2. Remediation Methods

Remediation method can be generally divided into two called in-situ and ex-situ based on where the remediation is carried out.

In-Situ	Ex-Situ
In situ ("in place") remediation refers to the cleanup of contaminated soils and groundwater without removing contaminated media from the subsurface, typically through the use of physical and/or chemical processes.	Ex-situ remediation involves the removal of contaminated media, either for off-site disposal or for on-site treatment and subsequent return to the subsurface.

It was decided to focus on in-situ remediation methods in this study because of the following reasons;

- Low risk of worker exposure to contaminants.
- Minimize ground disturbances.
- Applicable to soil while maintaining the facilities above ground.
- Easy even when there is limited availability of land.
- No drilling costs.

Therefore in situ remediation methods were studied in detail.

2.1. Electrokinetics Remediation

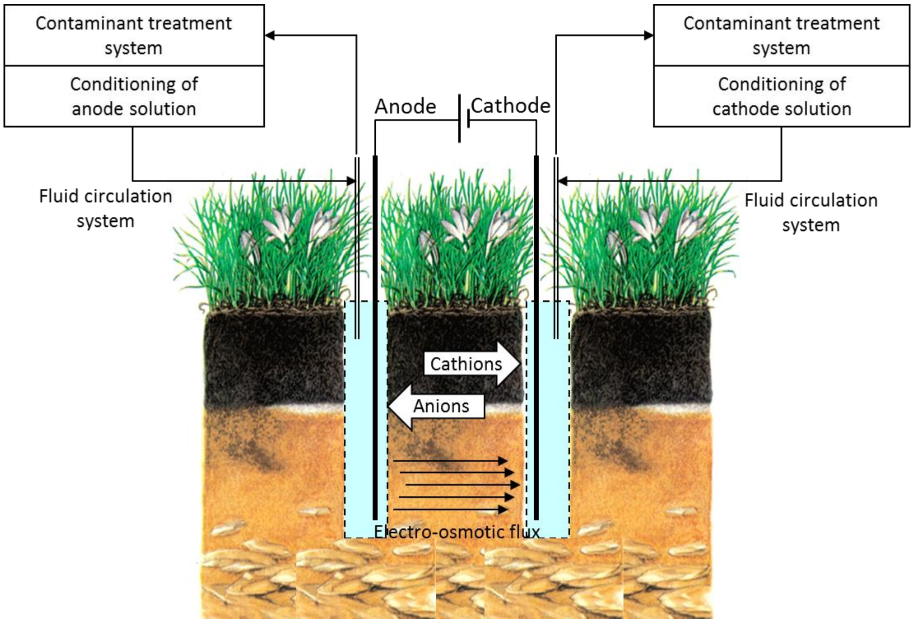


Figure 9: Electrokinetics remediation

Electrokinetics remediation (electrokinetics), is a technique of using direct electrical current to remove organic, inorganic and heavy metal particles from the soil by electric potential as shown in figure 9 above. The use of this technique provides an approach with minimum disturbance to the surface while treating subsurface contaminants. When current is applied, by the direct power source, to the electrodes, migrations occur beneath the soil surface. Although there are many types of migrations that occur in tandem with the current there are two driving migrations within electrokinetics; ionic migration and electrophoresis. When the electrolytic solution is injected within the soil part of the ionic solution forms a diffuse double layer with soils and contaminants. This diffused double layer will aid in the ionic drift that will occur as the current passes though the soil and surrounding liquid, this process is called electroosmosis. The thickness of the diffused double layer is a function of ionic composition of bulk solution and the average charge density of hydration products. As the electrolyte concentration increases the diffuse double layer thickness decreases. Electrophoresis is the mass flux of charged particles under an electric field. Both processes work at the same time but in a counter current manner. The charged particles driven by electrophoresis flow from the cathode to the anode while electrolytic solution flows from the anode to the cathode. Of the two main processes electrophoresis (or electromigration) is more dominant than electroosmosis. Electrophoresis serves as the driving factor that induces the flow of electroosmosis in the opposite direction. Electromigration also serves as the major component for ionic contaminant removal. For electromigration to occur absorbed material must be dissolved to an ionic form whether they are metals, organic or inorganic particles. Electroosmotic flow between the electrodes promotes the development of a low-pH environment in the soil. This low pH environment inhibits metallic contaminants from being sorbed onto soil particle surfaces which aids in the formation of compounds making electrokinetics possible. By this thought it is possible to acidify the soil and induce the release of absorbed heavy metals.

In this case current produced from heavy metals can be used and efficiency depends on degradation of heterogeneous soil. Although excavation is not required additional processes will be required for extracted waste.

2.2. Soil Flushing

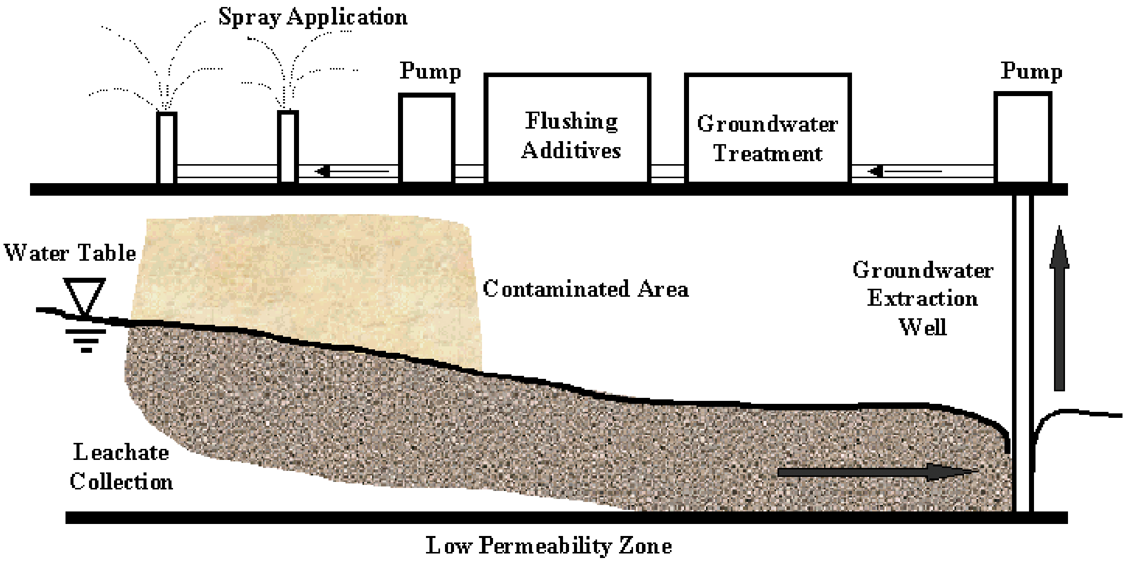


Figure 10: Soil Flushing

Soil flushing works by applying water to the soil as shown in the figure 10 above. The water has an additive that enhances contaminant solubility. Contaminants that are dissolved in the flushing solution are leached into the groundwater, which is then extracted and treated. In some cases, the flushing solution is injected directly into the groundwater. This raises the water table into the capillary fringe just above the surface of the water table, where high concentrations of contaminants are typically found. In many instances, surfactants (detergent-like substances) or solvents are used as the additive. The effectiveness of this process is dependent on hydrogeologic variables (type of soil, soil moisture etc) and the type of contaminant.

This process is however costly and failures in drilling of flow path can create serious issues by spread of contaminants.

2.3. Solidification/Stabilization

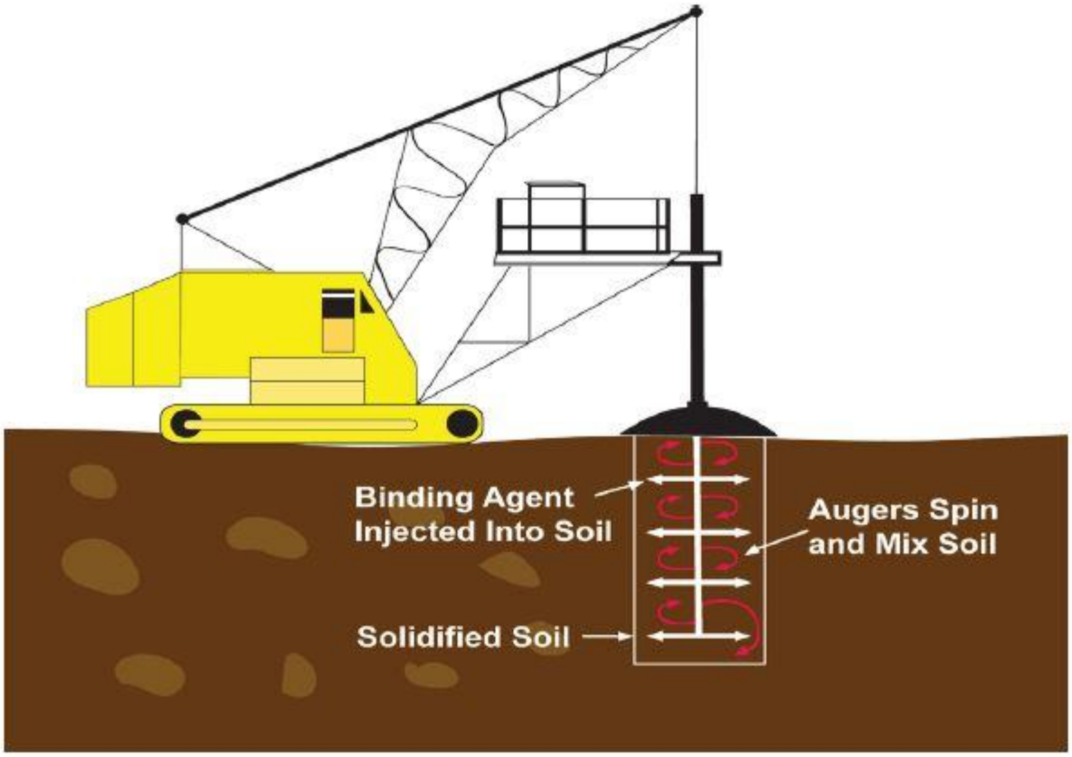


Figure 11: Solidification/Stabilization (Auger method)

Contaminants are physically bound or enclosed within a stabilized mass (solidification), or chemical reactions are induced between the stabilizing agent and contaminants to reduce their mobility (stabilization). Leachability testing is typically performed to measure the immobilization of contaminants. Solidification/Stabilization (hereafter referred to as S/S) techniques can be used alone or combined with other treatment as final or interim remedial measures. Auger(figure 11)/caisson systems and injector head systems are techniques used in soil S/S. They apply S/S agents to soil to trap or immobilize contaminants. Bottom barriers are horizontal subsurface barriers that prevent vertical migration by providing a floor of impermeable material beneath the waste. The installation of a grout injection bottom barrier involves directional drilling with forced grout injection. Implementation of this technology is highly dependent on the physical properties of soil.

Therefore this is an easy method to reduce risk without much change in physical properties of the contaminated soil.

Solidification/Stabilization is chosen as the best method out of the in-situ methods discussed above because it is economical and also because management is relatively easy although another method is required as secondary treatment.

Therefore solidification and stabilization will be studied in more detail

Advantages of Solidification/stabilization

- can be completed in a relatively short time period
- can be used to treat recalcitrant contaminants (heavy metals, PCBs, dioxins)
- may be performed in-situ or ex-situ
- process equipment occupies a relatively small footprint(better when limited land is available)
- the structural properties of the soil may be improved by treatment (strength, permeability)
- Applicable in residential areas
- Relatively economical
- Worker exposure to contaminants is low
- Generally eco-friendly

Chemical agents added to prevent leaching of heavy metals easily reduces mobility, thus creating a non-toxic environmentally friendly reactants. Two different methods of S/S are considered in the following table 3.

Table 3: Two methods of Solidification/Stabilization

FSM (iron based)	MKP (Phosphate based)
Greater solubility in water meaning higher applicability. High efficiency in Arsenic immobilization. In case of Pb initially shows high immobilization but this decreases with time.	Reaction is stable at wide range of pH values meaning formation of new minerals with low solubility. High efficiency for immobilization of lead.

Therefore it can be seen that for greater efficiency combination of remediation methods are required.

2.4. Phytoremediation

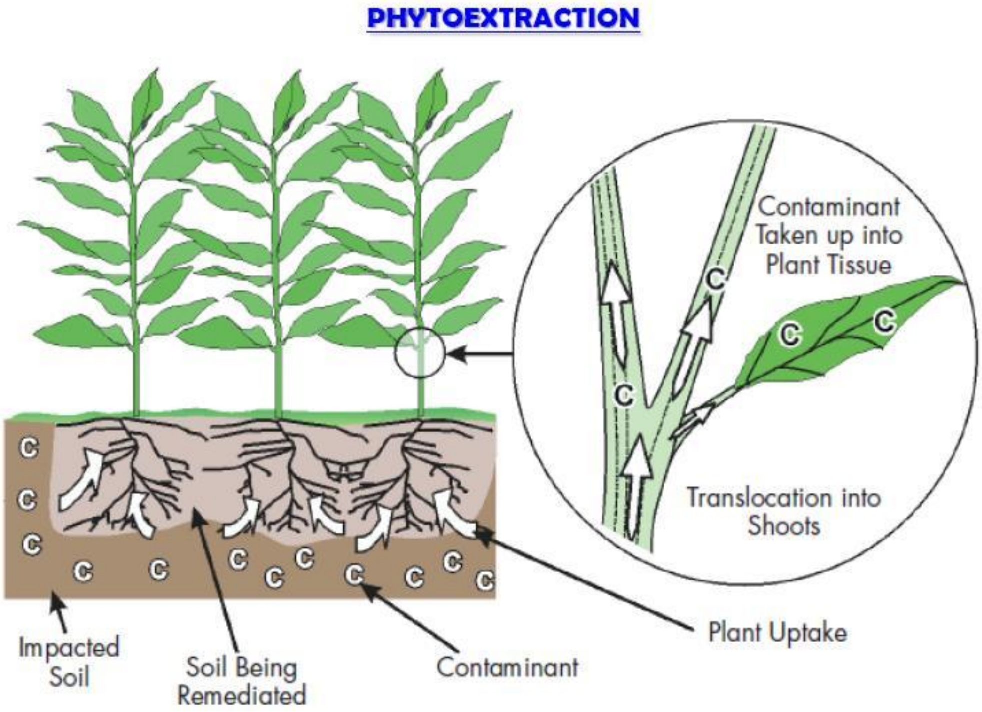


Figure 12: Phytoextraction

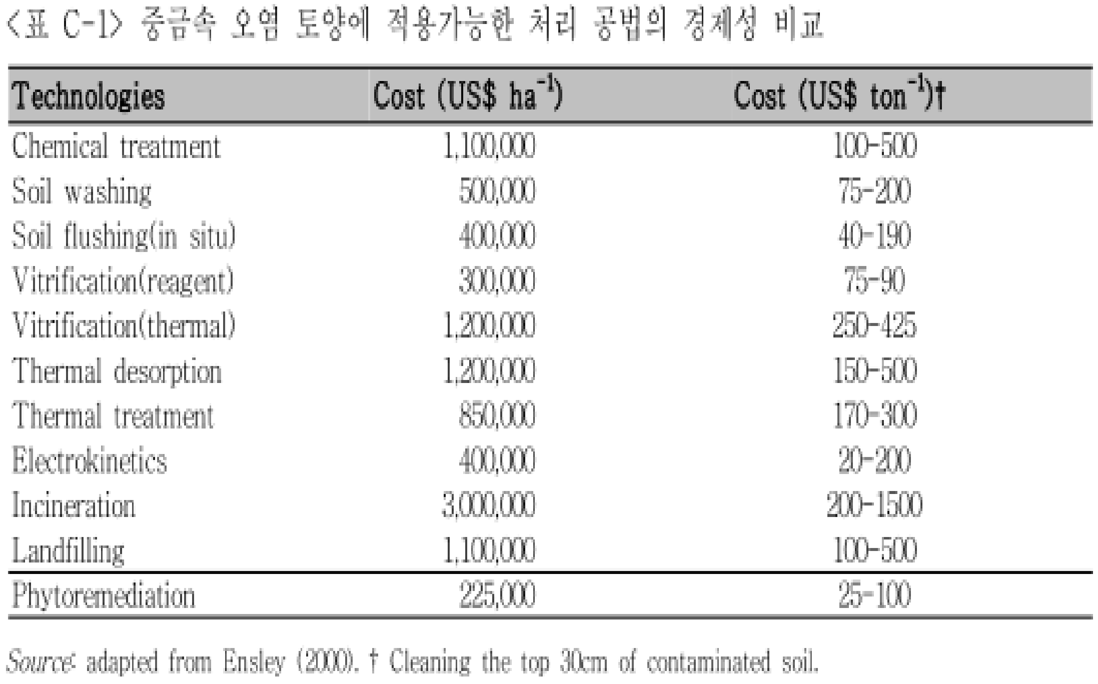
Phytoremediation is the treatment of environmental problems (bioremediation) through the use of plants that mitigate the environmental problem without the need to excavate the contaminant material and dispose of it elsewhere. **Phytoextraction** (figure 12) is a subprocess of phytoremediation in which plants remove dangerous elements or compounds from soil or water, most usually heavy metals, metals that have a high density and may be toxic to organisms even at relatively low concentrations. The heavy metals that plants extract are toxic to the plants as well, and the plants used for phytoextraction are known hyper accumulators that sequester extremely large amounts of heavy metals in their tissues.

Advantages

- This remedial practice is able to trap metal and radionuclide contaminates that are in mobile chemical forms. These forms are very dangerous and can be the most threatening to human and environmental health.
- Environmental disturbances are minimum(use of solar energy, clean)
- Eco friendly because low generation of by products
- In-situ method(no excavation required)
- Positive image among citizens therefore can be used in residential areas.

- Material handling is limited compared to other remedial strategies, such as excavation. Therefore costs are lower as shown in Table 4 below. (Only about 20% compared to other bioremediation methods and 10% of other physical/chemical methods)

Table 4: Costs for different remediation methods



〈표 C-1〉 중금속 오염 토양에 적용가능한 처리 공법의 경제성 비교

Technologies	Cost (US$ ha^{-1})	Cost (US$ ton^{-1})†
Chemical treatment	1,100,000	100-500
Soil washing	500,000	75-200
Soil flushing(in situ)	400,000	40-190
Vitrification(reagent)	300,000	75-90
Vitrification(thermal)	1,200,000	250-425
Thermal desorption	1,200,000	150-500
Thermal treatment	850,000	170-300
Electrokinetics	400,000	20-200
Incineration	3,000,000	200-1500
Landfilling	1,100,000	100-500
Phytoremediation	225,000	25-100

Source: adapted from Ensley (2000). † Cleaning the top 30cm of contaminated soil.

Oenothera tetraptera (Fourwing evening primrose)

Figure 13: Photo of fourwing evening primrose

Life time of Oenothera tetraptera (Fourwing evening primrose, hereafter referred to as FEP) is naturally 2 years and can be observed to grow in many different areas.

Advantages of using this plant in phytoextraction;

- Relatively large biomass.
- High seed production.
- The resistance to heat and dryness.
- Grows well naturally in mining area.
- Accumulation of large amounts of both arsenic and lead.

Characteristics of the FEP and characteristics of the land must be considered among other factors when deciding on the remediation method as shown in the figure 14 below.

Figure 14: Factors to consider when selecting phytoremediation method

The following table 5 shows that accumulation of As can be significantly increased by utilization of FEP in the process of phytoextraction.

Table 5: Factors that make FEP a good choice for As extraction

Increase of biomass promoting survival	Appropriate As concentration
Compost: improves water holding ability Fe 2 +: arsenic absorption activated. (Fe 2 + 1.8%, compost 6.9% max)	Smooth application below 100μM concentration of As.(In case of 50 μM can appear yellow) Accumulation upto 90, 900 μg / g in ground and below-ground.

Mycorrhizal inoculation	Sulfur treatment
Chemical similarity of As and phosphorus means Increase of As accumulation in body, Improvement of stability of plant form, biomass growth and increase of immunity.	Synthesis of Thiol group by concentration of 1mM of nutrient solution enhances Sulfur content making absorption of As increase by five times.

Therefore it can be concluded that for better results combination of short term remediation methods can be used with long-term remediation method, phytoextraction.

2.5. Conclusion on Remediation method selection

Table 6: Characteristics of selected methods

	Contaminated land	Target of Remediation	Labor and construction cost	Others
Soldization/ Stabilization (Aprox. 70,000 won/ton)	Total 110,000 m^2 1.3g/cm3 Applicable to all regions(Intensity of applicability differ)	Remediation period: Aprox. 40~20 days Short term: 60 ton / hour	Construction cost(excavators, injection machine), Labor,	FSM : 1wt% MKP : 2wt%
Phytoextraction (Aprox. 45,000 won/ton)	Total contaminated soil 20,000 m^2 No surrounding residential areas	Five to ten years, Long-term, low-cost treatment	Construction cost, Labor, Germination management labor	Requirements for Plant cultivation: Pig manure, Sulfur powder, Procurement of seeds, Irrigation

It was decided to use S/S method with phytoextraction as remediation methods in this study and the above Table 6 shows the summarization of the characteristics and applicability of those methods.

3. Evaluation and Conclusion

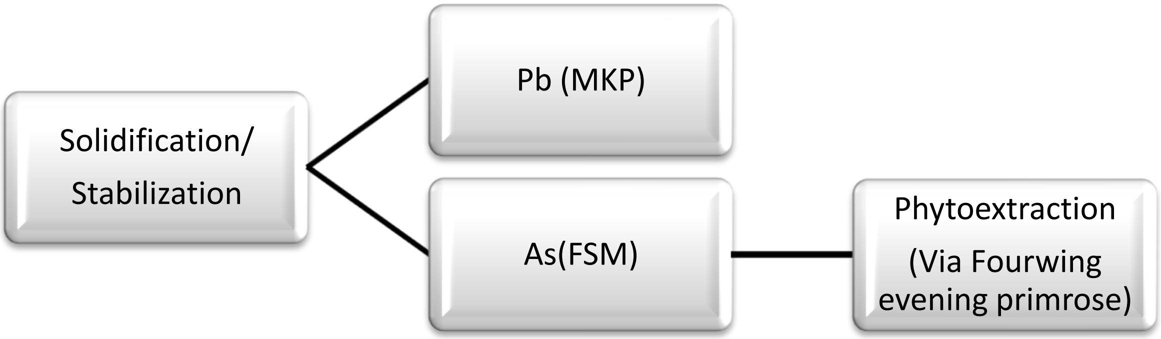


Figure 15:Summarization of Remediation Process

As shown above in the Figure 15 in the case of Lead, solidification and stabilization is sufficient. In the case of Arsenic apart from solidification and stabilization phytoextraction must also be employed. The following Figures 16 and 17 shows the predicted concentrations of Pb and As with time when these remediation methods are utilized.

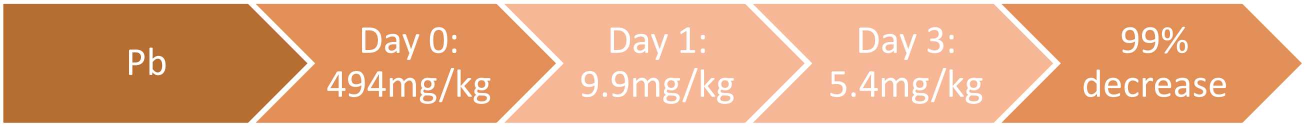


Figure 16: Concentration of Pb after S/S

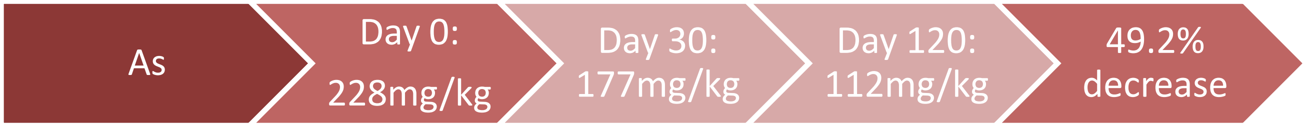


Figure 17: Concentration of As after S/S and phytoextraction

Thus effectiveness of the combination of the selected methods for remediation of heavy metals As and Pb in the studied area can be seen from the above figures. Pb can be effectively removed by the subprocess MKP of S/S method whilst As requires FSM of S/S as well as phytoextraction via fourwing evening primrose for efficient reduction of contamination in soil.