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공학석사 학위논문

**Reduction of Pb Leachability  
by Stabilization Using Fly Ash  
from Contaminated Soil of  
Ulaanbaatar in Mongolia**

플라이 애쉬를 사용한 안정화 기법으로  
몽골 울란바토르시 지역 납 오염토  
용출 감소 평가

2014년 8월

서울대학교 대학원  
건설환경공학부  
**Amarbayar Jugdernamjil**

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이 논문을 공학석사 학위논문으로 제출함  
2014년 8월

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## **Abstract**

# **Reduction of Pb Leachability by Stabilization Using Fly Ash from Contaminated Soil of Ulaanbaatar in Mongolia**

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The focus of this laboratory research is present the findings of a study on reduction of Pb leachability by stabilization using fly-ash from contaminated soil of Ulaanbaatar in Mongolia. Lead can be stabilized in soils based on two mechanisms which are lead precipitation and soil pH control. C-class fly-ash, Portland cement, quicklime can be used to treat trace element contaminated soil, reducing their mobility due to increased soil pH which enhances precipitation and adsorption, and also due to pozzolanic reactions and cementation. In the present study, the various additives

including Portland cement and quicklime with fly-ash and their various proportions were employed to stabilize Pb contaminated soil. All the Pb-contaminated 20 soil samples were obtained from 10 different locations (5 samples from gher district, 3 samples from multistoried administrative and residential building, 2 samples from industrial area) of Ulaanbaatar field. In each sample, there were collected top and sub soil sample. The concentration of Pb immobilization and effectiveness of the treatment were evaluated using the Toxicity Characteristic Leaching Procedure (TCLP) and maximum permissible concentration (MPC) of Pb in TCLP is 5mg/L. Additional leaching solutions, Simulated Acid Rain Solution (SARS) and deionized water were prepared with TCLP solutions to assess the leachable Pb in different leaching conditions. After leaching test, the pH measurement was performed in each sample. Also, the total Pb amount was evaluated Korean test method extraction of trace elements soluble in aqua regia. Harvard miniature compaction test was performed to estimate optimum moisture content for improving activity of chemical reaction between soil and additives. The unconfined compressive strength properties of the stabilized soils were measured to estimate the possibility of civil works and stabilization. The both of top soil and sub soil with fly-ash and cement mixture samples were showed highest amount of strength. Out of many

treatments, the soil with fly-ash, Portland cement and quicklime combination was shown most effective solution in every leaching solutions.

**Keywords:** Lead, Fly-ash, Harvard Miniature Compaction Test, Leaching solution, Unconfined Compressive Strength Test, TCLP, etc.

**Student Number:** 2011-22907

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# **Chapter 1 Introduction**

## **1.1 Background**

The rapid growth of the urban population is a global phenomenon, and Mongolia is not an exception. The influx of the population promotes the intense growth of the Mongolian capital and makes more complicated the ecological problems related to the development of the industrial sector of the economy and the growth of car parks. In the last 20 years, the capital's population has increased from 600 thousand to 1 million people (by 36–38 thousand per year); the number of cars has risen from 35 thousand to 95 thousands (about 6 thousand/year). More than half of the population of the country lives in Ulaanbaatar. The results of the ecological–geochemical survey fulfilled in the Mongolian capital in the 1990s needs corrections due to the social and economic changes in the country.

Ulaanbaatar is the capital and also the largest city of Mongolia. The climate is extremely continental with frequent temperature inversions in the winter. The mean annual precipitation in Ulaanbaatar is 240–260 mm; 60–90% is in July and August, and it is mostly of shower character. Mongolia has four season, the winter season is most longest season. It is located in the north-

central part of the country at an elevation of about 1350 m in the Tuul river valley, which is surrounded by mountains. The city was founded in 1639 and settled down at its current location 230 years ago. In 1986, Ulaanbaatar had a population of 500,200, i.e., nearly 25% of the nation's population. There were very few vehicles during this period; therefore, the soil pollution by heavy metals and other environmental problems in Ulaanbaatar were negligible.

Air pollution has become a significant environmental problem in the urban areas of Mongolia. In Ulaanbaatar, in particular, the environment has been deteriorating over the past 10 years. The primary sources of air pollutants in Ulaanbaatar include three coal-fired thermal power plants, which utilize about 400 low-pressure boilers and heating stoves; about 134,000 traditional "ghers" (Mongolian traditional dwellings); and over 100,000 automobiles. Following the rapid increase in the number of vehicles, the current auto transportation system has become overloaded, and traffic jams are a common occurrence. Corresponding to the rise in the number of vehicles, the concentration of nitrogen dioxide has also been increasing over the years. According to the statistics for February 2007, 70% of the total vehicles in Ulaanbaatar city have been in use for more than seven years; all these vehicles use leaded gasoline and diesel.

Therefore, the purpose of this research is to investigate a reduction of lead leachability by stabilization using fly ash with cement and quicklime from contaminated soil of Ulaanbaatar city.

## **1.2 Objectives and scopes**

The methodology to fulfill the objectives of the thesis work is to:

- Present the current condition of lead contamination of Ulaanbaatar area soil through the recent research.
- According to the recent research about heavy metal pollution of UB soil, it will be taken for this study
- Identify the usage of cost effective material for stabilizing additive to fit the situation of Mongolia (source, market, climate et al.,)
- Conduct laboratory tests to investigate the physical and chemical properties of before and after stabilization.
- Evaluate the optimum moisture content amount for improving chemical reaction of stabilization by Harvard miniature compaction test.
- Estimate the strength of stabilized soil samples for construction works.
- Evaluate the total lead content in the soil samples from Ulaanbaatar city area. Also, evaluate the total lead amount after treatment.

- Reduction of lead leachability by stabilization using fly ash with cement and quicklime from contaminated soil of Ulaanbaatar will be evaluated by toxicity characteristics leaching procedure.

## **Chapter 2 Literature Review**

### **2.1 Pb contamination of Ulaanbaatar city**

#### **2.1.1 General**

Lead (Pb) is one of the major environmentally hazardous pollutants belonging to toxic and carcinogenic heavy metals (HMs) of the first class of hazard. The major part of its compounds are characterized by low mobility and high accumulating capacity, which leads to its accumulation in a depositing environmental compartments and a negative effect on human health. Urban pollution with Pb among other HMs is being actively studied currently (Kosheleva et al., 2010; Kasimov et al., 2011; Pavlovic et al., 2004; Tomaševic et al., 2004); a number of studies are devoted to this element alone (Nikiforova et al., 2010; Wang et al. 2006; Chen et al., 2011). The problem of environmental pollution by lead is particularly relevant in Mongolia because it is one of the 17 countries still using leaded gasoline.

## **2.1.2 Environmental pollution with Pb from Ulaanbaatar city**

The average concentration of Pb in urban soils is 46 mg/kg , which is much smaller than, for example, in Belgrade with similar sources of pollution, it is 135 mg/kg (Tomaševic et al., 2004) or in Moscow, where it is 88 mg/kg (Nikiforov et al., 2010). However, the local values in Ulaanbaatar can reach 430 mg/kg.

The soils in the residential zones are the most contaminated ones. The violation of standards was observed in 29% of the multistoried building zone with concentrations of Pb of up to 430 mg/kg, and in the gher zone, about 60% of the area has a concentration of Pb of up to 300 mg/kg.

The supply of Pb in the residential zones is most often associated with local vehicular pollution, with an increased amount of exhaust gas during the cessation and the initiation of movement (Sawidiset al., 1995).

Pb concentration in the industrial and traffic zones is 2–3 times higher than background ones, and in 22% of the area.

The recreational zone is the least contaminated; no exceeding of the MPC was detected. Low concentrations of Pb in soils against an intense atmospheric contamination are due to high self purification potential of soils with high permeability and low sorption capacity.

The accumulation of Pb in the top soils is related directly to the amount of humus and physical clay (Kabata-Pendias, Pendias, 1989).

The map of Pb distribution in the top soils (Figure 2.1 ) confirms its preferential supply from the vehicle emissions. High concentrations of Pb are identified in top soils along the most congested roads with frequent traffic jams, especially in the city center (Sukhbaatar Square), between Peace Avenue and the Ring Road in the vicinity of the “Naran Tuul” market, at the intersection near the Palace of Officers, as well as in the northwestern part of the gher zone. The dependence of Pb accumulation in top soils on motor vehicle emissions was noted in the works of (Sawidis et al. 1995, Tomasevic et al. 2004, and HEI 2010).

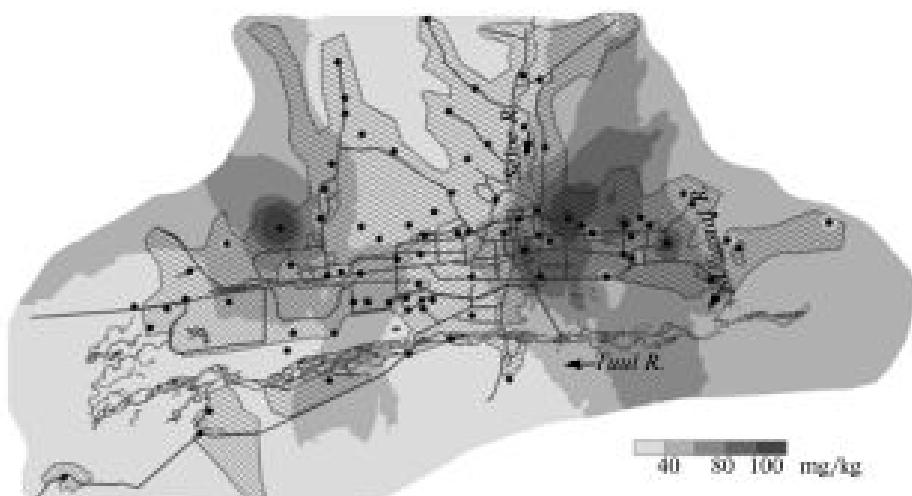


Figure 2.1. Concentrations of Pb in suspended matter of topsoil

The diurnal variation of Pb in the atmospheric aerosols was studied during the heating season, i.e., from December through March, on the territory of the Institute of Geography (Fig. 2). The largest one-time concentration of Pb in the atmosphere was observed in December 2008 and reached  $12 \mu\text{g}/\text{m}^3$  or 12 MPCot. In the other winter months, it was lower and amounted to 1.0- $7.0\mu\text{g}/\text{m}^3$  (1-7 MPCot). Surely, this is connected not only with the byproducts of coal combustion but also with the use of leaded gasoline containing lead tetraethyl. The peaks of Pb emissions during the day fall in the periods from 9 a.m. to 11 a.m. and from 8 p.m. to 11 p.m. (Figure 2.2 ). These very features of the diurnal variation have been noted also by Allen et al.(2011) in monitoring the particle matters in the atmosphere of Ulaanbaatar.

Heavy metals	Fe	Mn	Zn	Sr	Pb	Cd	Cr	Co	Cu	Ni	Hg
Max	4.62	793.4	558.1	845	533.4	4.8	373	26	68.22	84	1.9
Min	1.82	68.5	9.6	18. 3	5	0.1	4.8	0	1.5	055	0.024
Mean	2.77	447.3	52.4	364	55.7	1.85	89.4	6.5	44.4	30.0	0.352
Permissible limit	-	-	300	800	50	3.00	150	50	100	80	2.0

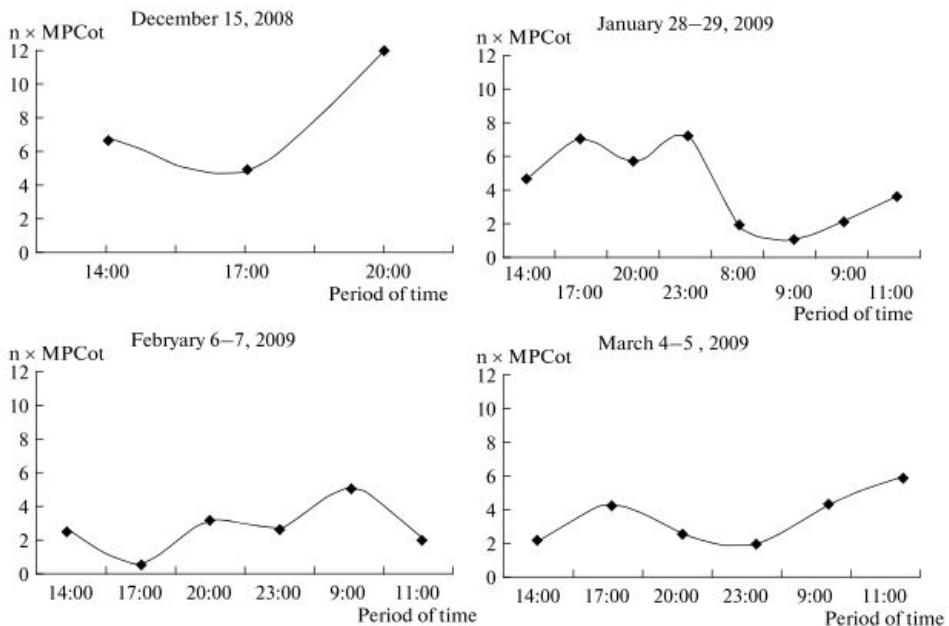


Figure 2.2. Diurnal patterns in Pb concentrations in the air of Ulaanbaatar

Table 2.1 Heavy metal contamination in Ulaanbaatar soil [mg/kg]

In from 2003 to 2007, the Mongolian Academy of Sciences has

reported heavy metal contamination in Ulaanbaatar soil as shown in Table 1.1. According to the results, the mean amount of Pb concentration was higher than permissible level. Also, the highest amount of Pb is 533.4 ppm.

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The comparison of the Pb concentration in whole city with their natural and urbanized background showed the higher 3.2 and 1.6 respectively (N.S.Kasimov et al. 2011)

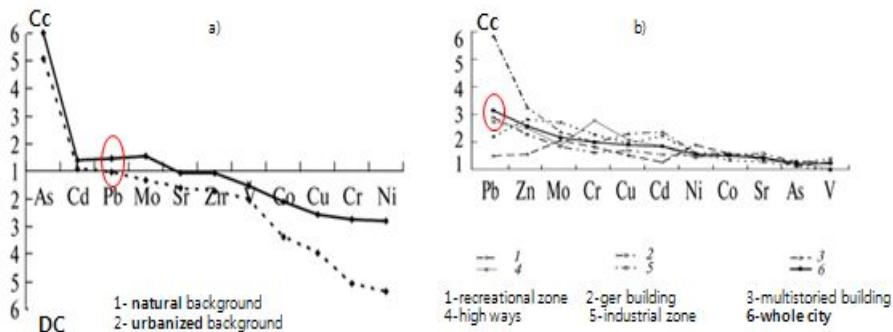
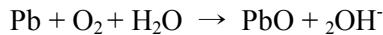


Figure 2.3. Geochemical specialization of the Ulaanbaatar soils.

## 2.2 Environmental problems of Pb contaminated soils

Pb has been used in gasoline, paint, batteries and cables. As a result of the widespread use of Pb over a long period of time, which element has caused several human health problems. Consequently, the risk to groundwater from leaching Pb has received increasing attention. Pb particles will be oxidized to be massicot, cerussite and hydrocerussite. Those Pb minerals are easy to be dissolved in an acidic condition and acid rain water.

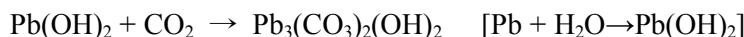
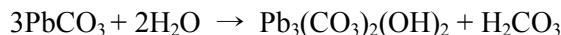
(1) Oxidation of Pb to massicot (PbO)



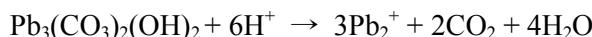
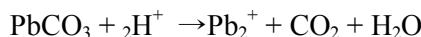
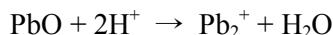
(2) Formation of cerrussite ( $\text{PbCO}_3$ )



(3) Formation of hydrocerussite ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ )



(4) Dissolution of Pb minerals



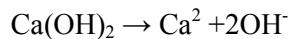
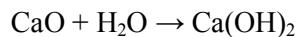
Pb in soils have various forms: water soluble, exchangeable, absorbed or chemically adsorbed, chelated, complexed and insolubly precipitated Pb (Ma and Rao, 1997; Lambert et al., 1997). Pb can cause environmental problems only if it becomes mobile and/or is ingested in the body of birds, wildlife, aquatic organisms or people. This can happen if Pb becomes: (1) dissolved or associated with fine suspended sediment particles in groundwater or surface water that people or wildlife drink, (2) eaten accidentally by wildlife while feeding on other things, mistaken for seeds, or picked up by birds as grit for the gizzard, and associated with dust particle that may be inhaled by human (NSSF, 1997)

## **2.3 Stabilization treatment principles**

When a significant quantity of lime is added to a soil–fly ash mixture, the pH of the soil–fly ash–lime mixture is elevated to approximately 12.8, the pH of saturated lime water. This is a very high pH compared to the pH of natural soil deposits, which are typically in the range of 5–8. The solubilities of silica, alumina, present in fly ash and clay minerals are greatly increased at this elevated pH levels, thus making them available for reaction with the calcium from lime and/or fly ash to form the cementitious hydrates, CAH and CSH. It is generally believed, that

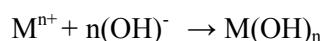
formation of these calcium aluminosilicate hydrates is mainly responsible for the high strength and low swell of the treated solids, as well as for heavy metal immobilization through surface sorption, inclusion and physical entrapment.

A simplified qualitative representation of some typical soil lime (pozzolanic) reactions is summarized below:

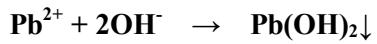


Where C = CaO, S = SiO<sub>2</sub>, A = Al<sub>2</sub>O<sub>3</sub>, and H = H<sub>2</sub>O. A wide variety of hydrate forms can be obtained, depending on reaction conditions, e.g., quantity and type of lime, soil characteristics, curing time and temperature.

Also, if CaO contact with water, it can release OH-(hydroxide). After that, OH<sup>-</sup> can remove Pb by precipitate.



M: Metal



## **2.4 Source of C-class Fly-Ash in Ulaanbaatar**

Thermal power plant number 3 and 4 are on activity among three coal-fired thermal power plants included in Ulaanbaatar, which produce much c-class fly-ash. Each TPP 3 and 4 makes approximately 107.000ton and 280.000ton c-class fly-ash.

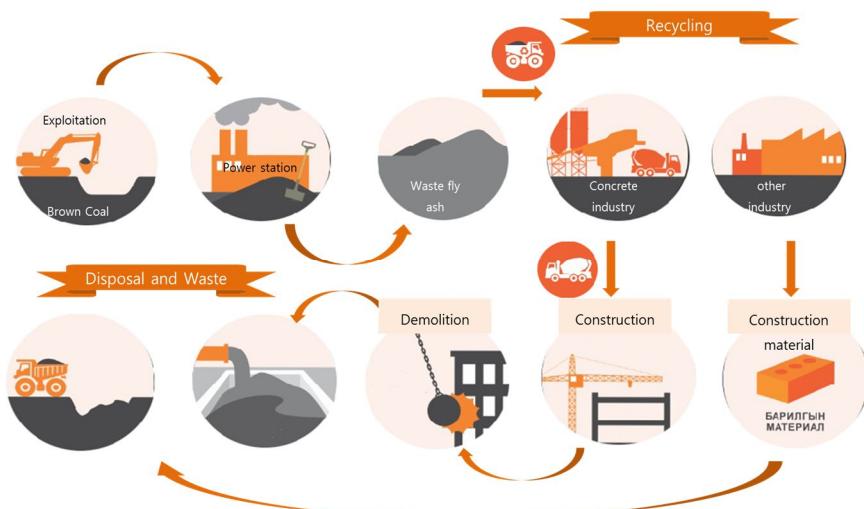


Figure 2.4. Scheme of class C fly ash

To compare with all-product amount of fly-ash, there are few amount in recycling for construction material and others. C-class fly-ash is almost waste and disposal in Ulaanbaatar (Journal of Environmental Sciences of Ulaanbaatar, 2013)

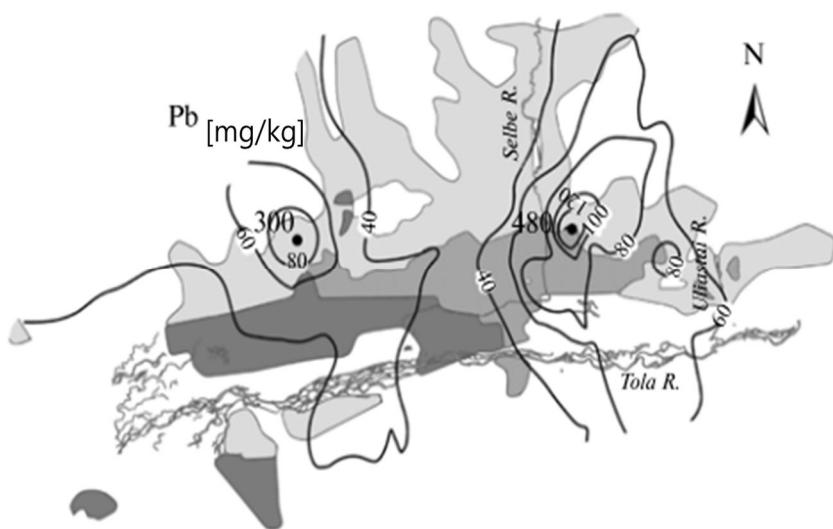
## Chapter 3 Materials and Methods

### 3.1 Materials

#### 3.1.1 Study area and soil sampling

All the soil samples were collected from 10 locations, 10 topsoil and 10 subsoil (under top soil), using hand auger and steel scoop and then stored in polyethylene bags. The collected soil samples were air dried for 24h and sieved through a 2mm stainless-steel sieve to remove large debris, stones, pebbles and others (MNS 3298 : 1990)

Figure 3.1. Distribution of lead contamination of UB



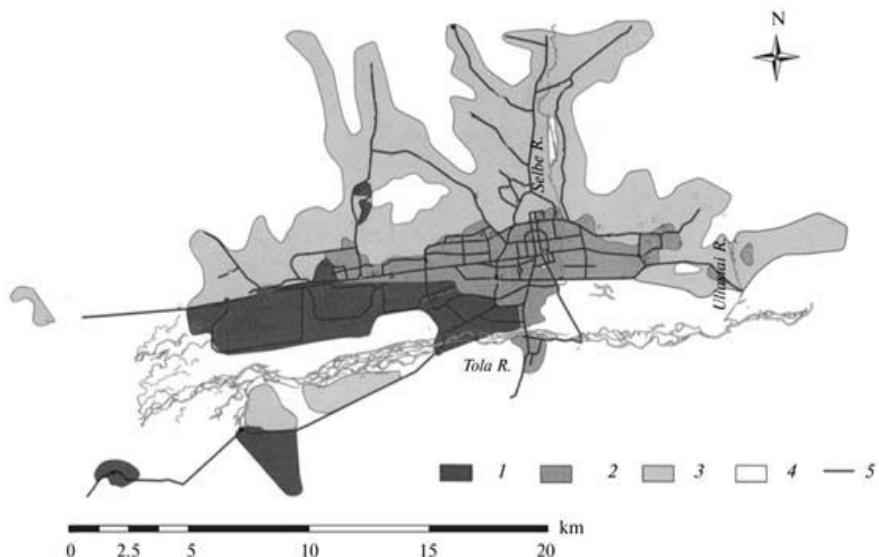


Figure 3.2. Functional zones map of Ulaanbaatar

Previous researchers (N.S.Kasimov et al. 2011) have divided map of Ulaanbaatar in 5 regions as shown in Figure 3.2.

#### FUNCTIONAL ZONES:

1. Industrial
2. Multistoried administrative and residential building
3. Gher building (traditional yurt house)
4. Recreational and undeveloped territories
5. Traffic

Depending on the previous researches (N.S.Kasimov et al. 2011), all samples were collected (May of 2013) from such as 6 soil samples from gher district, 2 soil samples from multistoried administrative and residential building, 2 soil samples from industry area.

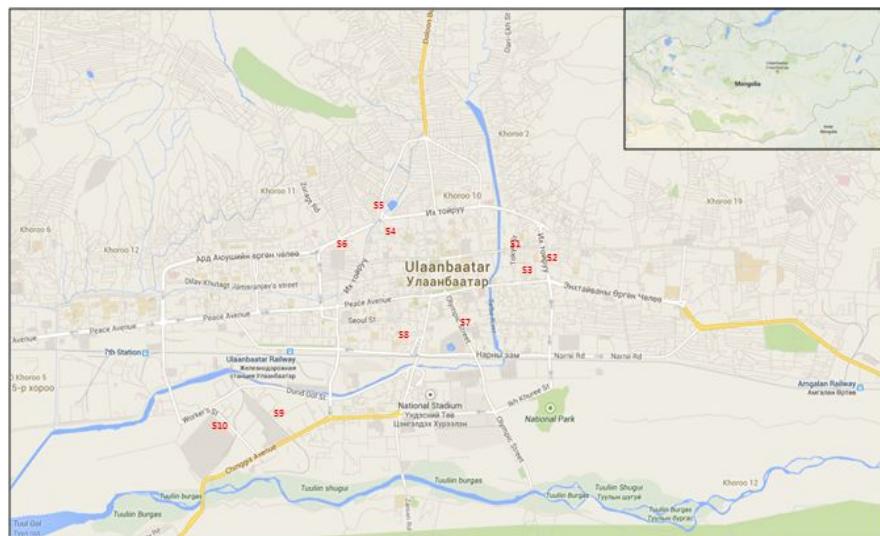


Figure 3.3. Location of sampling site of Ulaanbaatar, Mongolia

(Modified with Google Map)

### 3.1.2 Stabilizing additives

C-class fly-ash were obtained from Sampyo concrete industry in Seoul, Korea. C-class fly ash produced from the burning of younger lignite or subbituminous coal (Brown coal), in addition to having pozzolanic properties, also has some self-cementing properties. In the presence of water, Class C fly ash will harden and gain strength over time. Class C fly ash generally contains more than 20% lime ( $\text{CaO}$ ). Unlike Class F, self-cementing Class C fly ash does not require an activator. Alkali and sulfate ( $\text{SO}_4$ ) contents are generally higher in Class C fly ashes.



Figure 3.4. Image of stabilizing additives

Also, a Portland cement and quicklime were used to mix with fly-ash for enhancing stabilization. The mixing ratio determined as following:

Top Soil/Sub Soil +Fly Ash(10%)

Top Soil/Sub Soil +Fly Ash(5%)+Cement(5%)

Top Soil/Sub Soil +Fly Ash(5%)+Quicklime(5%)

TopSoil/Sub Soil +FlyAsh(2.5%)+Cement(2.5%)+Quicklime(5%)

2:1:1, $M_{\text{cement}} : M_{\text{flyash}} : M_{\text{quicklime}}$  by Yonghui Xi, (2009)

Table shows chemical composition of stabilizing additives were analyzed by X-ray fluorescence spectrometer (XRF-1700, Shimadzu). Each fly-ash, quicklime and cement have much high amount of CaO.

Table 3.1.The major elements of additives

Composition	Fly-ash	Quicklime	Cement
SiO <sub>2</sub>	33.2	1.20	23.6
Al <sub>2</sub> O <sub>3</sub>	25.3	-	7.1
Fe <sub>2</sub> O <sub>3</sub>	7.69	-	1.16
CaO	24.8	95.4	59.8
MgO	4.06	0.85	1.6
SO <sub>3</sub>	3.2	0.012	-
Na <sub>2</sub> O	1.9	-	-
K <sub>2</sub> O	-	-	0.96
TiO <sub>2</sub>	-	-	0.40
R <sub>2</sub> O <sub>3</sub>	-	0.75	-

## 3.2 Experimental procedure

### 3.2.1 Geochemical characteristics test

#### 3.2.1.1 Extraction of Pb soluble in aqua regia procedure

2.2.1.1 The aqua regia extraction method was used to determine the total heavy-metal content of the soil samples according to Korean standard test method modified by Jung-Seok Yang (2010) for soil.

1.5 grams of soil was added to a mixture of 10.5 mL concentrated hydrochloric acid and 3.5 mL nitric acid. Later, the stationary process was carried out for 2 hour to degrade the organic content, this was followed by heating for 2 h at 70°C. After cooling, the suspension was precipitated completely and then supernatant was collected. For determination of Pb concentration by Atomic Absorption Spectrometers, the supernatant was diluted 10 times with deionized water.

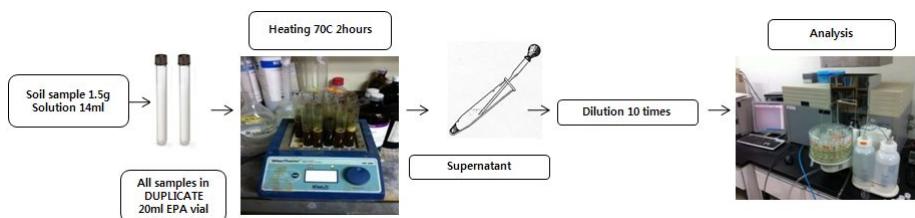


Figure 3.5. Experimental step of extraction of Pb soluble in aqua regia

### **3.2.1.2 Toxicity characteristic leaching procedure**

TCLP (US EPA method) is the most common leaching test used. It is the test most generally accepted by the U.S. EPA for leaching test and for determining toxicity under Resource Conservation and Recovery Act (RCRA). The TCLP is designed to evaluate the mobility of contaminants in municipal (sanitary) landfills in either liquid, solid, or multi-plastic materials. From a regulatory perspective, the TCLP is used to evaluate the leaching of metals, volatile and semi-volatile organic compounds, and pesticides, among other waste types, from waste categorized under RCRA as hazardous or toxic. The regulatory maximum critical level of Pb by TCLP is 5 mg/L.

Depending on the alkalinity of the material being tested, particle size that have been reduced to less 9.5mm are extracted with an acetate buffer solution of pH 5 or acetic acid solution of pH 3. The extraction fluid employed is a function of the alkalinity of the solids content of the waste sample. The solid sample is extracted with an amount of extraction fluid equal 20 times the weight of the sample. The extraction vessel, a polyethylene bottle, is then placed in a rotary agitator for 18 hours at 30rpm in a temperature controlled environment. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8  $\mu\text{m}$  glass fiber filter. Following collection of the TCLP extract, the pH of the extract should be recorded. Metals aliquots must be acidified with nitric acid to pH<2.

Extraction fluid will be prepared by the following procedures:

- (1) Extraction fluid # 1: Add 5.7 mL glacial CH<sub>3</sub>CH<sub>2</sub>OOH to 500 mL of reagent water, add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 5 + 0.05.
- (2) Extraction fluid # 2: Dilute 5.7 mL glacial CH<sub>3</sub>CH<sub>2</sub>OOH with reagent water to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 3 + 0.05.

Determination of appropriate extraction fluid will be performed by the following procedures:

- (1) Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask.
- (2) Add 96.5 mL of reagent water to the beaker, cover with a watch glass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1.

- (3) If the above of solution is  $>5.0$ , add 3.5 mL 1N HCl, slurry briefly, cover with a watch glass, heat to  $50^{\circ}\text{C}$ , and hold at  $50^{\circ}\text{C}$  for 10 minutes.
- (4) Let the solution cool to room temperature and record the pH. If the pH is  $<5.0$ , use extraction fluid #1. If the pH is  $>5.0$ , use extraction fluid #2.

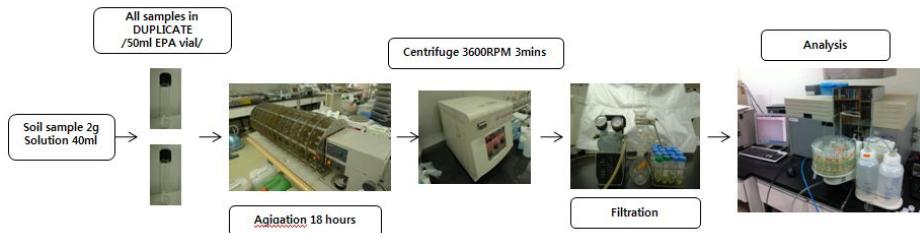


Figure 3.6. Experimental step of the leaching procedure

In case of evaluating the mobility of Pb in contaminated soils or treated soils, usually the modified TCLP test is used. As with the TCLP test, the TCLP modified was designed to quantify the mobility of the both organic and inorganic contaminants in solid samples. The TCLP modified does not require samples to be passed through a 9.5mm screen, to meet certain sample size (minimum 100mg), or to be certain surface area requirements prior to conduct of the leachability test. This test also differs from the standard TCLP in that it addresses treated waste or waste in produced solidified asphaltic or cementitious end products, which theoretically would withstand environmental stresses anticipated to be

encountered in a landfill. Other steps, such as preparation of leaching solutions, the ratio of solid to solution and experimental procedures, are the same with standard TCLP test. In this study, this modified TCLP test will be just called as TCLP test as many researchers did.

### **3.2.1.3 Preparation of Simulated Acid Rain Solution**

Acid rain is the term used to describe polluted rainfall. When the water vapor from the oceans and the land enters the atmosphere it is neutral in reaction i.e., non acid, pH 7, and is almost pure H<sub>2</sub>O. In the atmosphere, it mixes with variable amount of naturally occurring carbon dioxide (CO<sub>2</sub>) and sulphur (S) and forms weak acids. Depending on the amount of CO<sub>2</sub> and S present, the pH of the ensuing rainfall can be in the range 4-5. In the industrialized nations, the heavy combustion of fossil fuels (oil and coal) results in the emission of sulphur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>) into the atmosphere. Transformation of these gases into sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and nitric acid (HNO<sub>3</sub>) leads to further acidification of the water vapor. This artificial acidification of the cloud water results in an increase in the acidity of the precipitation, giving rise to regular occurrence of rainfall episodes with a pH around 4.0.

By far the largest contribution to this acid rain arises from oxidized H<sub>2</sub>SO<sub>4</sub> (62-79%) and most of the remaining acid is from oxidized HNO<sub>3</sub> (15-32%). In addition to these two main species, HCl (2-16%), also

produced by burning coal is found in the atmosphere (Schulz et al., 2000). To describe the real condition of acid rainfall at Ulaanbaatar area, the one Simulated Acid Rain Solution was prepared by adding the 60/40 weight percent sulfuric acid and nitric acid to distilled deionized water until the pH is  $4\pm0.2$ .

### **3.2.2 Geotechnical characteristic test**

#### **3.2.2.1 Harvard Miniature Compaction test**

Harvard Miniature Compaction test is for determining the moisture density relation of soils. In this apparatus, small quantity sample is compacted under kneading action of the spring loaded tamper set either at 10 kg or 20 kg. As the sample required is very small, a number of tests can be carried out, each time taking a fresh sample. The time required for compaction is very much less. The mould can be interchangeably used with Miniature Field permeameter where permeability tests can be conducted at high pressures.

In this study, the Harvard miniature compaction test was performed for determining the optimum moisture content in every sample. The OMC is for chemical reaction between soil particle with stabilizing additives.



Figure 3.7. Harvard miniature compaction facility

### **3.2.2.2 Unconfined Compressive Strength test**

In this study, UCS test has followed KS F 2314 and Dong-Ah facility was performed. The unconfined compression test is used to measure the shearing resistance of cohesive soils which may be undisturbed or remolded specimens. An axial load is applied using either strain-control or stress-control condition. The unconfined compressive strength is defined as the maximum unit stress obtained within the first 15% strain.

The purpose of the application of this test is to estimate strength of urbanized soil for civil works.



Figure 3.8 . Unconfined compressive strength facility

## Chapter 4 Results and Discussions

### 4.1 Result of Geotechnical Characteristics Test

#### 4.1.1 Harvard Miniature Compaction Test

The result obtained by Harvard miniature compaction test. Figure 4.1 shows relation between maximum dry density and optimum moisture content (OMC). In this experiment, there were tested at only top soil (TS), topsoil with fly-ash mixing (TS+F), topsoil with fly-ash and cement (TS+F+C), topsoil with fly-ash and quicklime, and combination. The topsoil was showed most high amount of maximum dry density than other mixing. When the maximum dry density has reached the peaks of every sample, it shows similar optimum moisture content around 12-13% at every sample.

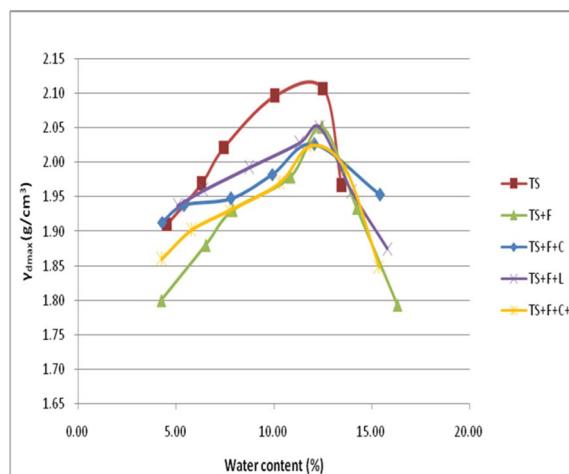


Figure 4.1. Result of the optimum moisture content in topsoil with additives

Only subsoil (SS), SS+F and SS+F+C were shown higher maximum dry density than others and also showed similar OMC around 13-14%. But SS+F+L and SS+F+C+L were shown higher OMC around 15% and maximum dry density was over  $1.85\text{g/cm}^3$ .

Both Top soil and Sub soil result show similar amount of OMC, but difference between maximum dry density amount due to coefficient of uniformity ( $C_u$ )

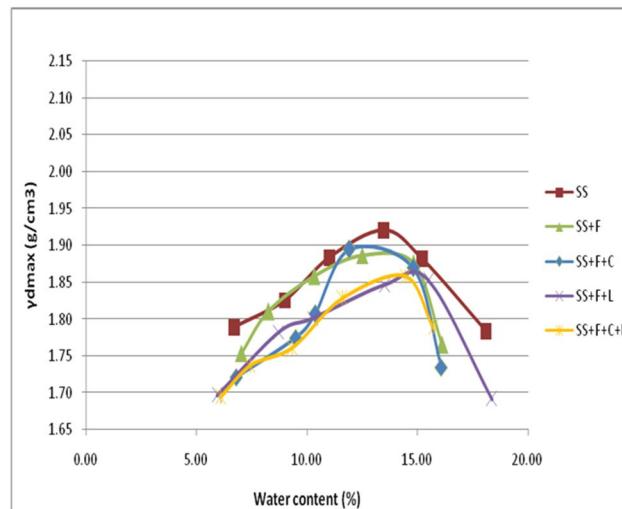


Figure 4.2. Result of the optimum moisture content in subsoil with additives

#### 4.1.2 Unconfined Compressive Strength

Figure shows that unconfined compressive strength test in topsoil mixed with other additives. TS+F+C mixture was shown high amount (more than  $0.35\text{kgf/cm}^2$ ) of stress than other samples due to using only cement for stabilization. As well, the only topsoil was shown most low amount of stress. Both of TS+F+C+L and TS+F+C were shown similar stress amount below  $0.35\text{kgf/cm}^2$ . Mixture of topsoil with fly-ash was shown less amount because of not enough existence of CaO than cement and quicklime. Fly-ash has not much cementitious behavior to compare with cement and quicklime.

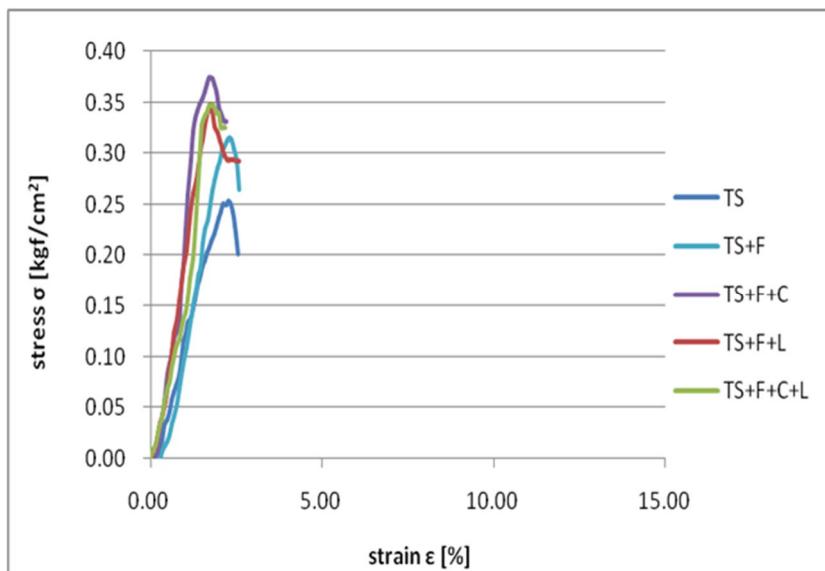


Figure 4.3. Result of unconfined compressive strength test  
in topsoil with other additives

In this result, the subsoil and additives with subsoil were under the unconfined compressive strength test. It was shown same case as topsoil which is high stress amount showed by SS+F+C. But SS+F and SS+F+L were shown similar stress amount each other and less than combination.

There were not significant variation between topsoil sample and subsoil sample in unconfined compressive strength due to both of sample showing similar physical behavior.

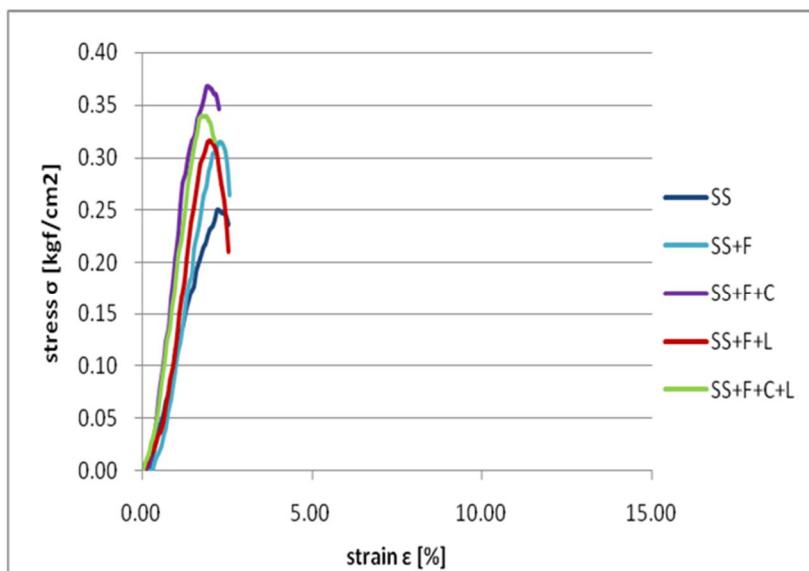


Figure 4.4. Result of the unconfined compressive strength test  
in subsoil with other additives

## **4.2 Result of Geochemical Characteristics Test**

### **4.2.1 pH variation of before and after stabilization**

Figure shows the pH variation between after and before remediation in every sample by Korean standard method KS I ISO 10390. The combination of all additives makes to increase the pH after treatment. The pH of combination shows alkalinity in except TCLP-pH3. In both of SARS-pH4 and DI-pH6, all mixtures were shown increasing of pH. But there were slightly increasing in TCLP-pH3 and TCLP-pH5 because of strong acid used for making solution.

Because of using pozzolanic materials, it makes to increase the pH amount. If the pH is higher (range of alkalinity), it works available on stabilizing process completely.

Both of the subsoil and topsoil were shown similar pH variation as well. But topsoil was shown small amount than subsoil in SARS-pH4.

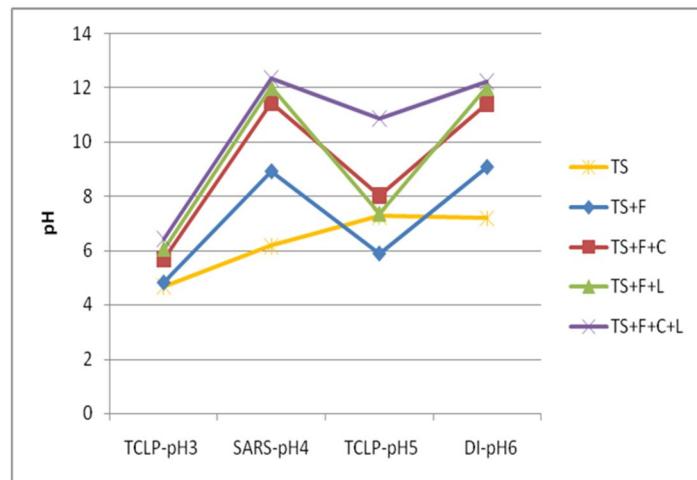


Figure 4.5. Result of the pH variation in topsoil with additives.

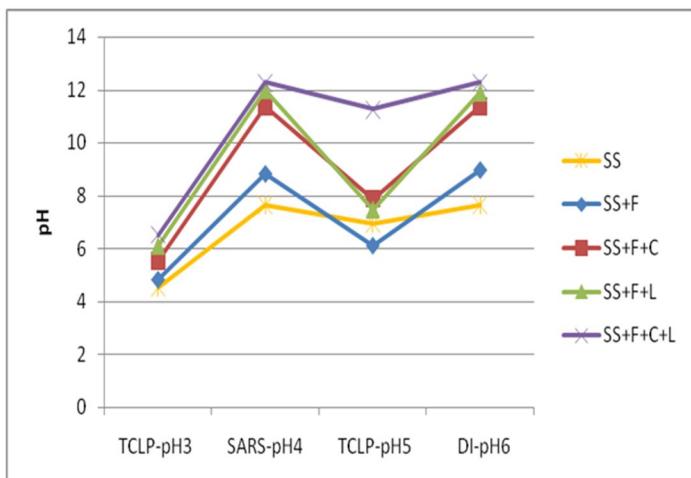


Figure 4.6. Result of the pH variation in subsoil with additives.

#### **4.2.2 Extraction of Pb soluble in aqua regia**

A total 20 samples (included 10 topsoils, 10 subsoils) were estimated for their total Pb content by Korean test method-Extraction of heavy metal soluble in aqua regia. Depending on the atomic adsorption spectrometer result, A samples number of S1t, S1s, S2t, S2s, S3t, S3s, S4t, S4s were shown higher than permissible limit of Pb is 100mg/kg (MNS 5850:2008)

Table 4.1. Permissible level of Pb contamination in soil [mg/kg]

Element	Soil type			Max. level
	Clayey soil	Loamy soil	Sandy soil	
Pb (lead)	100	70	50	100
(MNS 5850:2008)				

In this study, to focus on the much higher amount of Pb polluted soil sample S1t and S1s. The leaching test was performed in S1s and S1t.

Both of S1t and S1s were shown 596 mg/kg and 567 mg/kg respectively. According the result of S1t and S1s, the concentration of Pb is 5 times higher than permissible limit.

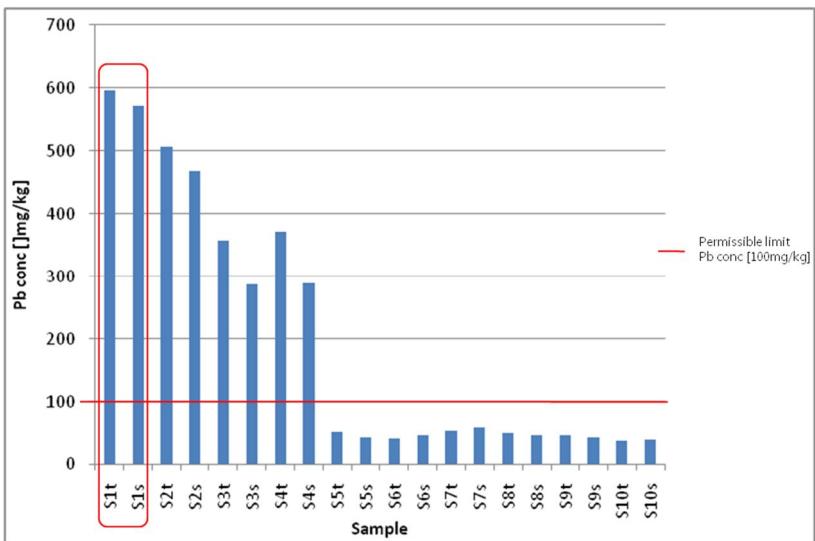


Figure 4.7. Total Pb content of samples from functional zones of UB

Also, the total Pb content test was performed in before and after remediation. Both figures show the no significant changes between after and before remediation. But there were slightly decreasing in after treatments is shown. After treatment, there are still much than permissible limit because of using an aqua regia solution. Which is very strong acid content and it breaks stabilizing between particle and stabilizing additives.

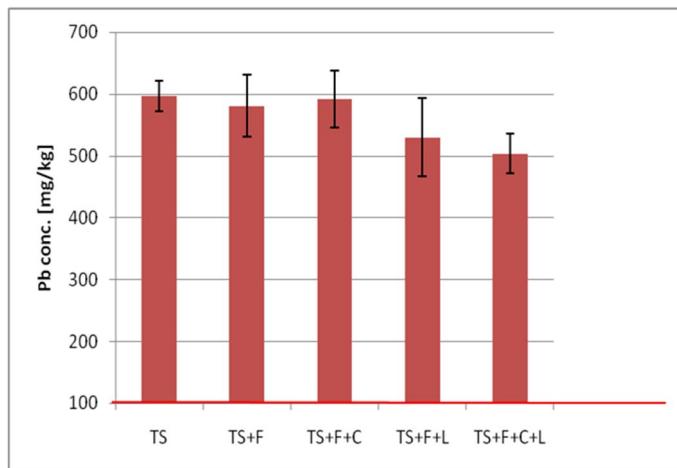


Figure 4.8. Result of total Pb content in topsoil and mixtures

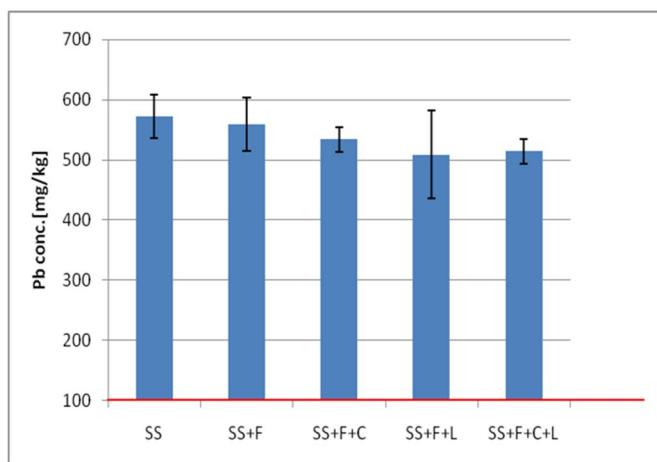


Figure 4.9. Result of total Pb content in subsoil and mixtures

#### 4.2.3 Toxicity characteristic leaching procedure

The result shows the variation of Pb leaching between before and after stabilization at every TCLP-pH3, SARS-pH4, TCLP-pH5, DI-pH6 solutions. Among the result of all solutions, a TCLP-pH3, SARS-pH4, TCLP-pH5 were shown higher amount of Pb before remediation except the DI-pH6. The combinations of TS+F+C+L and SS+F+C+L were most effective in all conditions less than permissible limit 5ppm by EPA-TCLP.

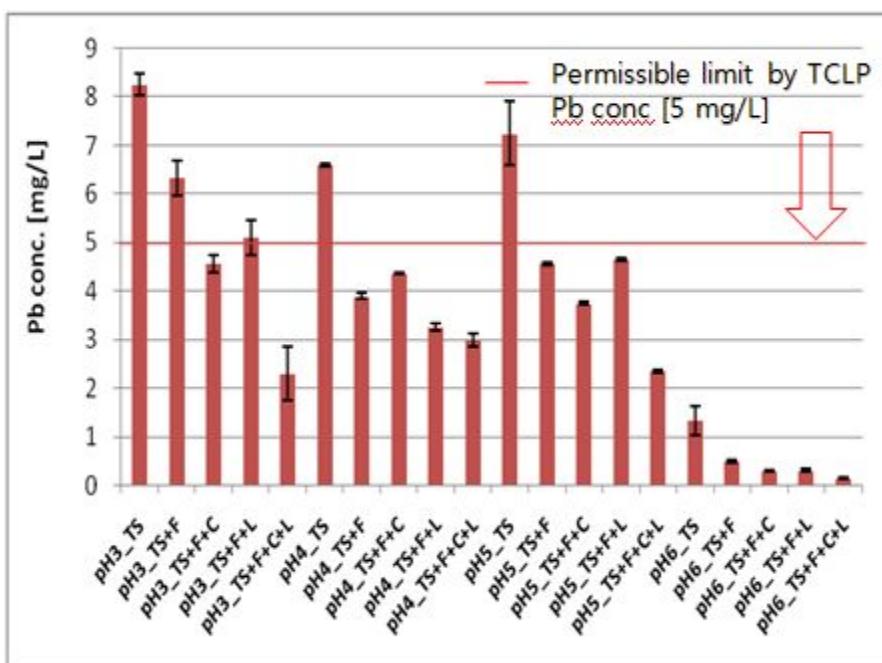


Figure 4.10. Result of Pb leaching test in top soil and other mixtures

In result of subsoil and other mixtures, both of TCLP-pH3 and TCLP-pH5 were high amount of Pb than permissible limit before stabilization. Also, the combination of SS+F+C+L was most effective than other mixtures. For example, the before stabilization amount in SS is 7.5 ppm at TCLP-pH3. At the after stabilization, it was decreased from 7.5 ppm to 2.5 ppm. Only C-class fly ash using stabilization is not effective material in the Pb contamination than mixed other additives.

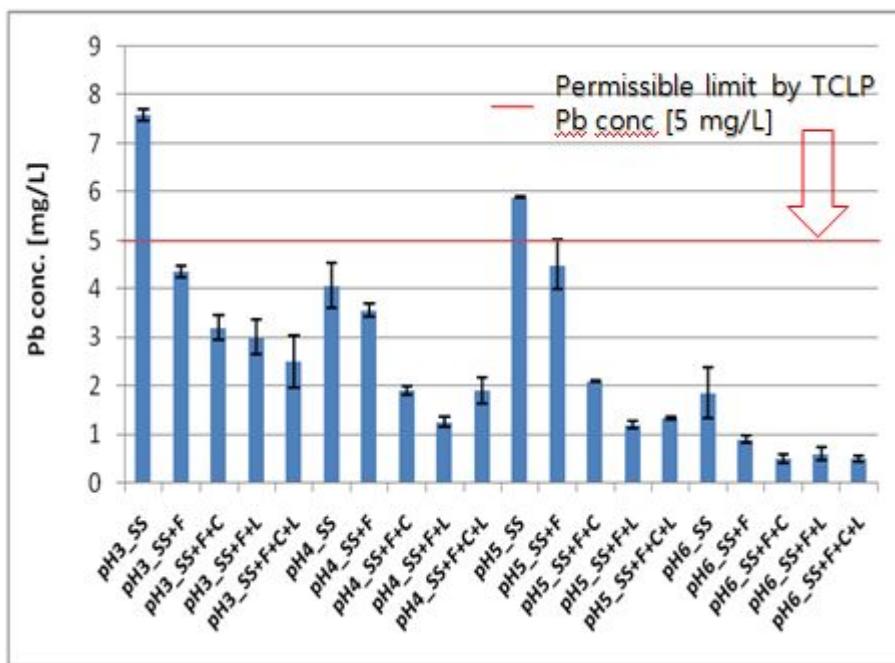


Figure 4.11. Result of Pb leaching test in subsoil and other mixtures

## **Chapter 4 Conclusions**

The peaks of Pb emissions during the day fall in the periods from 9 a.m. to 11 a.m. and from 8 p.m. to 11 p.m. during from December through March.

The average concentration of Pb in urban soils is 46 mg/kg. The soils in the residential zones are the most contaminated ones. The violation of standards was observed in 29% of the multistoried building zone with concentrations of Pb of up to 430 mg/kg, and in the gher zone, about 60% of the area has a concentration of Pb of up to 300 mg/kg.

. The topsoil was showed most high amount of maximum dry density than other mixing. When the maximum dry density has reached the peaks of every sample, it shows similar optimum moisture content around 12-13% at every sample.

Only subsoil (SS), SS+F and SS+F+C were shown higher maximum dry density than others and also showed similar OMC around 13-14%.But SS+F+L and SS+F+C+L were shown higher OMC around 15% and maximum dry density was over 1.85g/cm<sup>3</sup>.

Both Top soil and Sub soil result show similar amount of OMC, but difference between maximum dry density amount due to coefficient of uniformity (Cu)

TS+F+C mixture was shown high amount (more than 0.35kgf/cm<sup>2</sup>) of stress than other samples due to using only cement for stabilization. As

well, the only topsoil was shown most low amount of stress. Both of TS+F+C+L and TS+F+C were shown similar stress amount below 0.35kgf/cm<sup>2</sup>. Mixture of topsoil with fly-ash was shown less amount because of not enough existence of CaO than cement and quicklime. Fly-ash has not much cementitious behavior to compare with cement and quicklime. There were not significant variation between topsoil sample and subsoil sample in unconfined compressive strength due to both of sample showing similar physical behavior.

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A samples number of S1t, S1s, S2t, S2s, S3t, S3s, S4t, S4s were shown higher than permissible limit of Pb is 100mg/kg. In this study, to focus on the much higher amount of Pb polluted soil sample S1t and S1s. The leaching test was performed in S1s and S1t.

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Also, the total Pb content test was performed in before and after remediation. Both figures show the no significant changes between after and

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Among the result of all solutions, a TCLP-pH3, SARS-pH4, TCLP-pH5 were shown higher amount of Pb before remediation except the DI-pH6. The combinations of TS+F+C+L and SS+F+C+L were most effective in all conditions less than permissible limit 5ppm by EPA-TCLP.

In result of subsoil and other mixtures, both of TCLP-pH3 and TCLP-pH5 were high amount of Pb than permissible limit before stabilization. Also, the combination of SS+F+C+L was most effective than other mixtures. For example, the before stabilization amount in SS is 7.5 ppm at TCLP-pH3. At the after stabilization, it was decreased from 7.5 ppm to 2.5 ppm. Only C-class fly ash using stabilization is not effective material in the Pb contamination than mixed other additives.

## Bibliography

Sorokina, O.I., Kosheleva, N.E., Kasimov, N.S., Golovanov, D.L., Bazha, S.N., Dorzhgotov, D., Enkh-Amgalan, S., 2013, Heavy metals in the air and snow cover of Ulan Bator, Geography and Natural Resources., 34(3), 291-301.

Sorokina, O.I., Enkh-Amgalan, S., 2012, Lead in the landscapes of Ulaanbaatar city (Mongolia), Arid Ecosystems, 2(1), 61-67

Kasimov, N.S., Kosheleva, N.E., Sorokina, O.I., Bazha, S.N., Gunin, P.D., Enkh-Amgalan, S., 2011, Ecological-geochemical state of soils in Ulaanbaatar (Mongolia), Eurasian Soil Science, 44(7) , 709-721

Tserennyyam, B., Enkhtur, O., Kitae, B., Jung-Seok, Y., 2010, Assesment of metals contamination of soils in Ulaanbaatar, Mongolia, Journal of Hazardous Materials, 184(2010), 872-876

Kosheleva, N.E., Kasimov, N.S., Dorzhgotov, D., Bazha, S.N., Gunin, P.D., Golovanov, D.L., Enkh-Amgalan, S., Batkhishig, O., 2011, Soil pollution with heavy metals in the industrial cities of Mongolia, Mongolian Journal of Biological Sciences, 9(1-2), 39-45

Toxicity characteristic leaching procedure, U.S-EPA method 1311, 1992

Multiple extraction procedure, U.S EPA method 1320,1986

Soil quality- pH measurement, KS I ISO 10390:2005

Soil quality- Pretreatment of samples for physic-chemical analyses, MNS ISO 11464:2002

Environmental protection- Soil- General requirements on the probe for analytical purposes

MNS 3298:1990

Soil quality- Extraction of trace elements soluble in aqua regia,  
KS I ISO 11466:2008

Soil quality- Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc in aqua regia extracts of soil- Flame and electrothermal atomic adsorption spectrometric methods,

KS I ISO 11047:2009

Korean standard test method for unconfined compressive test of soils,  
KS F 2314:2013

Soil quality- Soil pollutants elements and substance  
MNS 5850:2008

Korean test method for particle size distribution of soils  
KS F 2302:2002

Christina, S., Anthimos, X., Ioannis, P., 2002, Reduction of Pb, Zn and Cd availability from tailings and contaminated soils by the application of lignite fly-ash, Water, Air and Soil Pollution, 137, 247-265

Jang, A., Kim, S.I., 2000, Technical note solidification and stabilization of Pb, Zn, Cd, and Cu in tailing wastes using cement and fly-ash, Minerals Engineering, 13, 14-15

Jurate, K., Anders, L., Christian, M., 2007, Stabilization of Pb and Cu contaminated soil using coal flyash and peat, Environmental Pollution, 145, 365-373

Hyunjin, S., Sehjong, K., Junboum, P., Assessment of Pb contaminated soils taken from a small arms firing range in South Korea

Ganjidoust, H., Hassani, A., Rajabpour, A., 2009, Cement based solidification stabilization of heavy metal contaminated soils with objective of achieving high compressive strength for the final matrix, Civil

Engineering, 16(2), 107-115

Yongsik, O., Jungeun, L., Deokhyun, M., 2011, Stabilization of Pb and Cd contaminated soils and soil quality improvements using waste oyster shells, Environ Geochem Health, 33, 83-91

Jungseok, Y., Juyong, L., Youngtae, P., Kitae, B., Jaeyoung, Ch., 2010, Soil pollution characteristics of metallic mine area according to extraction methods, 한국지하수토양환경학회지, 15(3), 1-6

Chunyang, Y., Hilmibin, M., Md Ghazaly, Sh., 2006, Stabilization solidification of lead contaminated soil using cement and rice husk ash, Journal of Hazardous Materials, 137(2006), 1758-1764

Dermatas, D., Xiaoguang, M., 2003, Utilization of fly-ash for stabilization solidification of heavy metal contaminated soils, Engineering Geology, 70(2003), 377-394

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Tserennym, B., 2009, Stabilization of metal contaminated soils using Mongolian natural zeolite, Kumoh National Institute of Technology

Deokhyun, M., Jury, L., Dennis, G.G., Jeonghun, P., 2010, An assessment of Portland cement, cement kiln dust and class C fly ash for the immobilization of Zn in contaminated soils, Environ Earth Sci, 61, 1745-1750

Yonghui, X., Xiaofeng, W., Hao, X., 2000, Solidification stabilization of Pb-contaminated soils with cement and other additives, Tongji University

Kogbara, R.B., 2014, A review of the mechanical and leaching performance of stabilized/solidified contaminated soils, Environ. Rev., 22, 66-86

정선우., 2012, 몽골 올란바타르 인위적 배출원에 의한 수은 오염 평가, 서울대학교 에너지시스템공학부

Alpaslan, B., Yukselen, M.A., 2002, Remediation of lead contaminated soils by stabilization solidification, Water, air and soil pollution, 133, 256-263