Thesis for the Degree of Master of Science

Study of Lime Treatment as a Stabilization Process applied to Arsenic and Other Heavy Metals Contaminated Soil around Abandoned Mines

by

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Department of Applied Geology
The Graduate School
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February, 2006

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토양 개량제를 이용한 폐광산 주변 비소 및 중금속 오염토양의 안정화 공법의 적용

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Study of lime treatment as a stabilization process applying to arsenic and other heavy metal contaminated soil around abandoned mine

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Abstract

Most of abandoned mines in Korea are contaminated by arsenic and other heavy metals originated from mine tailing and waste ore rock fragments. Continuous leaching heavy metals to the sub-surface by rainfall contaminated groundwater and surface water, and also generated their accumulation in farmland products at contaminated sites. Objective of this research is to decrease the heavy metal leaching rate from contaminated soil by using lime treatment. Batch and pilot scale column experiments were performed for the lime treatment and arsenic contaminated soils of Goro abandoned mine, Korea were used. Five amendments, such as CaO, $CaCO_3$, lime, limestone and apatite were applied for experiments, and various amounts of amendment were used (0, 2, 5 and 10 wt% of soil). Leaching rate of heavy metals with the addition of soil amendments was stabilized within one day and thus 3 day was decided to the maximum shaking time for batch experiments. From the result of batch experiment, four amendments, except apatite, lowered more than 20 times of As leaching rate (50 times in maximum) from soils, suggesting that

these amendments are very useful to prevent As extraction from contaminated soils. The decreasing pattern of Cd, Pb and Zn concentration in leaching solution was similar to that of As in batch experiments.

Pilot scale column experiment was performed to investigate the decrease of metal extraction rate from soil by lime treatment. Granulated and powdered lime were used as stabilizing materials to decrease the extraction of heavy metals. The uncontaminated soil mixed with lime was covered on the contaminated soil in the column ("capping soil treatment") and the contaminated soil mixed with the granulated lime ("mixing soil treatment") were applied for column experiments. Extraction rates of heavy metals from each column experiment were calculated and compared with those of the column test without lime treatment. Heavy metal extraction rate of granular lime treatment was similar to that of powdered lime treatment. In case of adding lime (5wt%), Cd extraction rate decreased to more than 157 times, compared with initial extraction rate. From results of pilot scale column experiments, mixing soil treatment process by using lime had a great efficiency to decrease As, Cd and Zn extraction rate from contaminated soil. For 5wt% of lime mixing treatment, As concentration of drain water was 10ppb and it decreased less than 0.5ppb after 1 year extraction. Cd and Zn concentrations also decreased 200-400 times within few months in case of 10 wt% granular lime mixing treatment. The efficiency of stabilization for heavy metals with "Mixing soil treatment" was higher than that with "Capping soil treatment". Because of its low cost, high

efficiency, and easy operation, the lime treatment would be one of major processes to control heavy metal contaminated soil.

Key words : Arsenic, stabilization, lime, soil remediation, abandoned mine, heavy metal contamination.

CHAPTER 1. INTRODUCTION

High concentration of heavy metals such as cadmium, lead, zinc, mercury, nickel and arsenic in soils may cause long term risks to ecosystem and humans. Although heavy metals were released in varying quantities into soils from parent materials, increasing environmental contamination has been caused by human activities, such as mining, smelting, fossil fuel combustion, agricultural practices and waste disposal (Ross, 1994; Alloway, 1995). Most of area nearby abandoned mines in Korea were contaminated with arsenic and other heavy metals from mine tailing and waste ore rock fragments (Lee et al, 2003). Continuous leaching of these metals to the sub-surface by rainfall contaminated groundwater and surface water, and also generated their accumulation in farmland products at contaminated sites.

One of main processes to control heavy metal contaminated soil was to decrease the extraction or leaching rate of heavy metal by using of soil stabilizing materials, called "stabilization method". One of the cheapest and the most effective material for stabilization was lime (Palfy et al, 1998). Lime-based stabilization/solidification could be an effective remediation alternative for the immobilization of arsenic or other heavy metals in contaminated soils. This research focused on the soil stabilization process by using lime to decrease the extraction of arsenic and other heavy metals from contaminated soils around abandoned mines.

CHAPTER 2. OBJECTIVE

Objective of this study is to investigate the stabilization method as a remedial process for arsenic and other heavy metal contaminated soil nearby abandoned mine, by determining available soil amendments and designing operating conditions of the stabilizing process.

This research was divided to three major parts shown below.

1) Determination of available amendments used for soil stabilization method to apply arsenic and other heavy metal contaminated soil by batch experiment

2) Evaluation of optimal stabilization conditions to reduce leaching rates of arsenic and other heavy metals by batch experiment

3) Investigation of the capability of the lime treatment to real site application by "capping soil treatment" and "mixing soil treatment" by pilot scale column experiments

CHAPTER 3. BACKGROUND

3.1 Outline of research area

3.1.1 General statement

Research area is bound to soils beside of the main stream connected to Goro abandoned Zn-mine, which is located at the Gunwi county, Korea. Goro mine had been activated from 1950 to 1980 and about 30,000 tons of mine tailings and waste rock fragments had been left at the storage site, which was 200m down away from the mine entrance. The construction of a dam across the main stream connected the Goro mine is under contemplation by the government and the lineal distance between the dam and the Goro mine is about 12km. The study area is shown in Fig. 1. Arsenic and other heavy metals extracted from soils and flowed from the upper area of a dam site could be the main source to contaminate water when a dam is built. Therefore, arsenic and other heavy metals extraction should be decreased by the application of soil remediation methods. In this research, the soil stabilization method using lime (CaO) was applied to decrease the extraction of arsenic and other heavy metals from soils. The remediation of arsenic and other heavy metals contaminated soils in this area should be immediately performed on account of following reason,

(1) to lower heavy metals concentration of groundwater and (2) to preserve stream from arsenic and other heavy metals contaminated soil.

3.1.2 Geological characteristic

The geological constitution of research area was mostly composed of Cretaceous rocks such as Hamman Formation, Banyaweol Formation, Chunsan Formation, and Sinyangdong Formation in the Silla Formation Group of Kyongsang Supergroup. They were mostly igneous rocks such as rhyodacite rocks, rhyolitic breccia, rhyolite porphyrite, granite porphyry, andesite rocks, and granite rocks (Cha, 2004, Do, 2005). Quarternary alluvial sediment layer distributed around valley or stream around Goro mine were mostly composed of gravels and sands. Fig. 2. shows the geological map of the study area (Korea Water Resources Corporation, 2002).

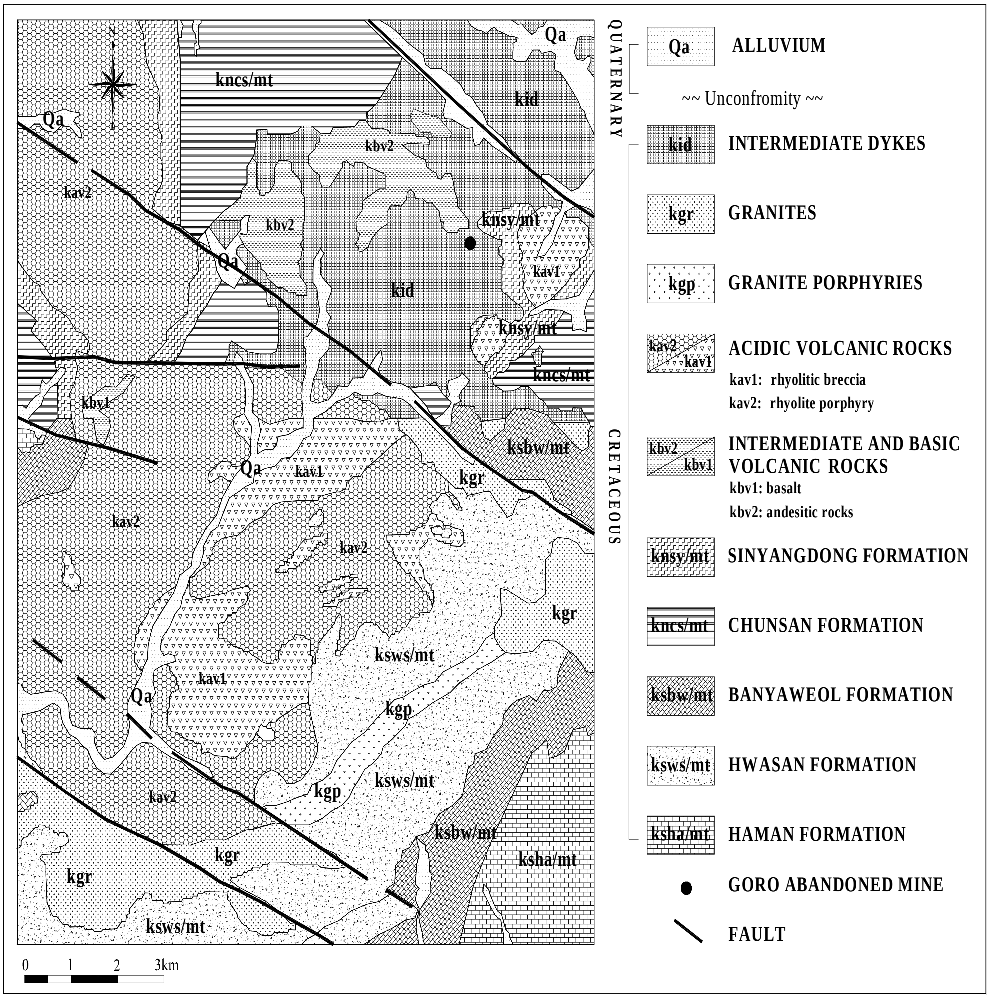


Fig 2. Geological map of the study area (Korea Institute of Geoscience and Mineral Resources, 2004).

3.2. Arsenic and heavy metals

3.2.1 Arsenic

Arsenic, a naturally occurring element, is ubiquitous in the earth's crust and widely distributed in soil (median concentration of 6mg/kg with a typical range of 0.1~40mg/kg) and water (average in fresh water : 1~10㎍/L) (Tamaki and Frankenberger, 1992; Azcue, 1995). Over 200 arsenic-containing minerals have been identified, with approximately 60% being arsenate, 20% sulfides and sulphosalts and the remaining 20% including arsenides, arsenites, oxides and elemental arsenic (Onish, 1969). The natural sources of arsenic in soils are mainly oxysalts and S containing minerals. The range of Eh and pH in soils can lead to either As(Ⅴ) or As(Ⅲ) with microbial activity causing methylation, demethylation and/or change in oxidation state and the presence of S species may, if the redox potential is low enough, favour the formation of arsenic sulfide minerals (Moore et al,1988). Arsenic, as well as other elements or compounds, can be redissolved from the soil due to acid precipitation or complexation with ligands from waste waters (Mari and Pentti, 1997). Toxicity and mobility of arsenic in the environment are dependent on the chemical form or species in which it exists(Richard, 1998). The toxicity of arsenic is related to the oxidation state of the element. Elementary arsenic is not toxic, As(Ⅲ) is 25 to 60 times as toxic as As(Ⅴ) and several hundred times as toxic as methylated arsenic compounds, and arsine is the most toxic compound of arsenic compounds (V. Dutre et al, 1995).

3.2.2 Cadmium, lead and zinc

Under most oxidation-reduction conditions, these elements exist in solution as divalent or trivalent cationic species (G. Nelson Eby, 2004). Brookins (1988) gives a number of calculated Eh-pH diagrams for virtually all systems of geochemical interest. At high pH, many of these elements form insoluble oxyhydroxides or, in the presence of carbonate, insoluble carbonates.

In its natural form, cadmium is relatively rare and concentrated in argillaceous and shale deposits as greenockite (CdS) or otavite ($CdCO_3$) and is usually associated with zinc, lead or copper in sulfide form (Cameron,1992). It is more mobile, though, than zinc at low pH, particularly at pH values between 4.5 and 5.5. Above pH 7.5, cadmium is not very mobile. A natural source of cadmium is volcanoes that can release cadmium into the atmosphere, spreading it over a wide area.

Lead is found naturally in soils, most commonly in the form of the ore galena (PbS) and in smaller quantities in cerussite ($PbCO_3$), angelsite ($PbSO_4$) and crocoite ($PbCrO_4$). Lead can be found in soils at the surface and organic matter in higher quantities. In general, background levels less than 10ppm are found, and mobility of lead in soils is low (Jawarsky, 1978).

Although not as toxic as cadmium, zinc is quite often associated with this metal. Soil texture, pH, nature of the parent rocks and organic content all affect the natural content of zinc in the soil. Under acidic conditions, zinc is usually divalent and quite mobile. At high pH, zinc is bioavailable due to the solubility of its organic and mineral colloids.

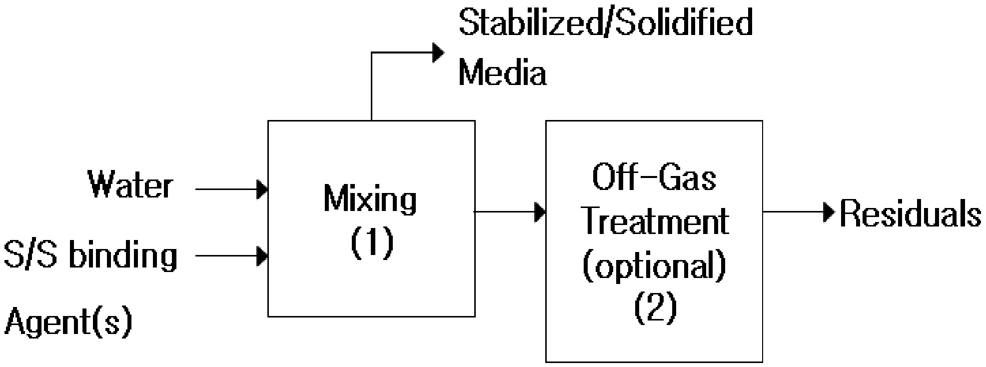
3.3. Principle of stabilization method

In general, solidification/stabilization technology is considered a last approach to the management of hazardous waste. The aim of its technique is a strong fixation of contaminants in soil medium to reduce leaching rate. Heavy metals which extracted from contaminated soils around abandoned mine, affect the quality of groundwater and surface water. Therefore, the decrease of leaching rate is the most important factor to apply the stabilization method. Stabilization is the process that reduces the mobility of the hazardous constituents of a waste or that makes the waste easier to handle. Most of stabilization techniques aimed for the immobilization of metal-containing wastes are based on additions of cement, water glass, coal fly ash, lime and gymsum (Malone et al., 1982; Wiedemann, 1982; Goumans et al., 1991) (Fig.3).

Immobilization techniques can treat a large amount of wastes in-situ and prevent its interaction with environment (Xu, Zhou et al., 2005). Among them, in-situ chemical immobilization is the remediation technique that decreases the concentration of dissolved contaminants by sorption or precipitation (Basta and McGowen, 2004). While physico-chemical extraction techniques generally imply the degradation of soil structure and high costs, stabilization techniques can improve soil physico-chemical and biological properties, do not generate by-products, are less expensive and therefore are more suitable for remediation of extensive areas of low-contaminated land (Mench et al., 2003). The technique is based on the use of amendments to accelerate those processes (sorption, precipitation and complexation reactions) that take place naturally in soils to reduce mobility and bioavailability of trace elements (Bolan and Duraisamy, 2003; Hartley et al., 2004).

The principal advantages of stabilization are economy, versatility and speed. Stabilization uses technology familiar to most civil engineering contractors and yields a “value added” product that can be used as bulk fill in earthworks or as a foundation material for redevelopment. It also allows the development of site-specific mixtures and appropriate methods of mixing for a wide range of situations (J.M. Reid et al., 1999).

In this study, the efficiency of lime (CaO) as a stabilizing material to reduce the heavy metal extraction rate from soil was investigated by batch and column experiments. Batch experiments were performed to determine available amendments and to investigate the decrease of extraction from soil in the stabilization method. Pilot scale column as a physical model for the genuine contaminated soil environment was designed and heavy metal extraction rates by artificial rainfall were measured in diverse treatment conditions. "Capping soil treatment" known as the process overlying the non-contaminated soil mixed with lime on the contaminated soil and "Mixing soil treatment" known as the process mixing contaminated soil with lime were applied to decrease heavy metal extraction in the column experiment.



In situ S/S Process

Fig. 3. Schematic of typical S/S processes (USEPA, 1993d).

CHAPTER 4. EXPERIMENTAL METHOD

4.1 Sample analysis of heavy metals contaminated soil at Goro abandoned mine

Eighty kilograms of surface soils were collected at around the stream valley connected to the Goro abandoned mine (Fig. 4). After the pre-treatment process, according to KSAM (Korean Soil Analysis Method), concentration of As and other heavy metals (Pb, Cd and Zn) were analyzed on Inductively Coupled Plasma (ICP/AES : Perkin elmer, Optima 3300XL) and Atomic Adsorption Spectrometer (AAS : Perkin elmer, AAnalyst 200). Soil samples were dried in oven at 35℃ for 2-4 day and sieved at 2mm in diameter. For the analysis of Cd, Zn, and Pb, ten gram of soil sample was mixed with 50ml of 0.1N HCl in a glass flask and was shaken with 100 rpm at 20℃ for 60 minutes in thermohydrostat. For As, ten gram of soil sample was mixed with 50ml of 1N HCl in a glass flask and was shaken with 100 rpm at 20℃ for 30 minutes in thermohydrostat. Solution in the flask was filtered by filter paper (5B) and analyzed on ICP/AES or AAS.

Fig. 4. Sampling site on the Goro abandoned mine.

4.2 Measurement of soil sample properties

Physical and chemical properties of soil samples such as pH, Eh, and grain size directly affect extraction properties of heavy metals from soils. Eh and pH of contaminated soil were measured by electrometer (Istek, 815PDC). Particle distribution of soils was also measured through the dry-sieving and pipetting method and the principle component analysis was performed by X-ray fluorescence spectrometer (Shimadzu, XRF-1700).

4.3 Selection of stabilizing amendment

Selection of stabilizing amendment is important because it directly controls the leaching rate of heavy metal contaminated soils. In this study, five amendments, such as CaO, $CaCO_3$, lime, limestone and apatite were applied for experiments. Amount of amendment also affects the stabilization efficiency of heavy metals, and various amount of amendments were used in the experiment (0, 2, 5 and 10 wt% of soil). Powdered amendments were used in batch experiments and granulated amendments were used in column experiments.

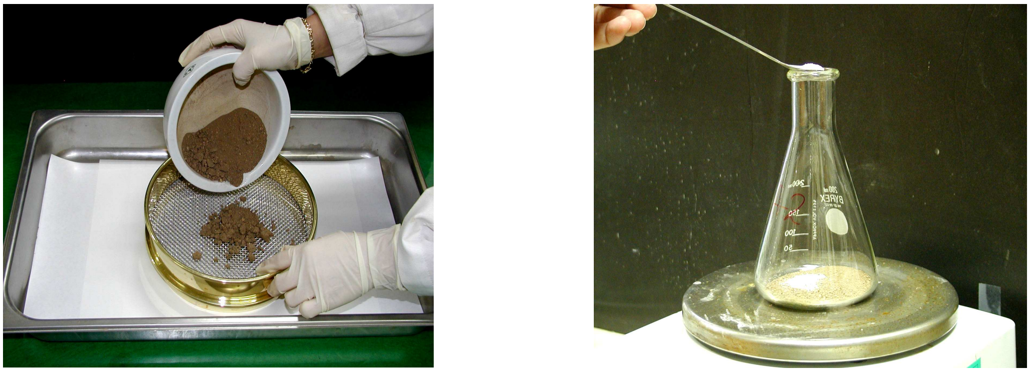
Table 1. Contents and species of amendment used in stabilization experiment

	Contents of amendment mixed with contaminated soil		
Species of amendment	[1]Lime 2wt%	Lime 5wt%	Lime 10wt%
	[2]Limestone 2wt% (from parent rock)	Limestone 5wt%	Limestone10wt%
	[3]Apatite 2wt% (from parent rock)	Apatite 5wt%	Apatite 10wt%
	[4]$CaCO_3$ 2wt% (refined powder)	$CaCO_3$ 5wt%	
	[5]CaO 2wt% (refined powder)	CaO 5wt%	

* 1 and 2 : from HANIL COMPANY
* 3 : from made in CHINA
* 4 and 5 : from SHINYO PURE CHEMICALS CO. LTD (ACS grade)

4.4 Batch experiment

Soil samples were dried at 35℃ and sieved with No. 10 mesh (2mm in diameter). Each amendment (Lime, Limestone, Apatite, CaO or $CaCO_3$) was mixed with contaminated soil at various ratio, and mixed with deionized water, titrated at pH 6. Mixing solution in 100ml flask was capped and shaken at 20℃ and 100 rpm in the thermohydrostat. While the flask was shaken, 10ml of equalized solution was sampled every 12hr, 24hr and 72hr. It was centrifuged, and filtered by filter paper (5B) for heavy metal analysis on ICP/MS (Fig. 5).



(a) Sieving of contaminated soil (b) Addition of amendments

(c) Shaking at thermohydrostat (d) Separating in centrifuge

(e) Filtering of supernatant (f) Analysis on ICP/MS

Fig. 5. Batch experiment for the efficiency of stabilization process.

4.5 Evaluation for the leaching rate of contaminated soil with the "capping treatment" in pilot scale column experiments

The objective of stabilization process was to reduce leaching rate of heavy metals passing through soil to groundwater. Pilot scale column experiments with an artificial rainfall were performed to investigate the decreasing rate of heavy metal extraction by using the "capping treatment". Contaminated soil of 27kg collected at Goro mine and un-contaminated soil of 27kg for capping soil treatment were dried at 1:1 ratio (wt%). Acryl column (18.9cm in diameter and 30cm in height), which of the upper and lower part consist of dense lattice screen plates and the drain system for injection and extraction of artificial rainfall, was designed. The average amount of rainfall per month around Goro mine was 91.2mm per unit area, which was determined as artificial rainfall quantity. Thirty three percent of average monthly rainfall in Goro area was injected into the column for 30 days. One day of the column experiment represented to one month duration in the field condition.

Each column was packed with Ottawa sand (1cm in thickness) at the bottom of column and the upper layer of Ottawa sand was packed with contaminated soil (approximately 10cm in thickness). Capping materials, which were mixed with un-contaminated soils and amendments, covered on the contaminated soil layer (approximately 10cm in thickness). The amount of soil and amendments for the experiment was shown in Table 2. Fig 6. shows the column experiment for the capping treatment.

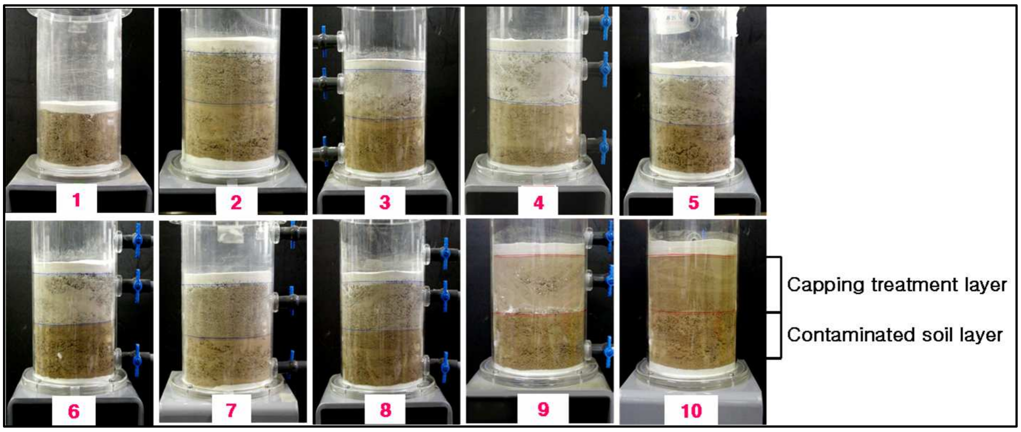
Table 2. The amount of contaminated soil, un-contaminated soil and amendment for capping experiment

For contaminated soil	Area of column	268.8cm^2
	Column thickness of contaminated soil	10cm
	Soil wet bulk density	1.38kg/m^3
	Total amount of contaminated soil	**3.76kg**
For un-contaminated soil	Area of column	268.8cm^2
	Column thickness of un-contaminated soil	10cm
	Soil wet bulk density	1.38kg/m^3
	Total amount of un-contaminated soil	**3.76kg**
For amendment	2wt% of amendment	**77g**
	5wt% of amendment	**198g**

At every 12hr, 817.15ml of artificial rain was injected to the top of the column and discharged water was sampled from the bottom of the column (Fig. 7). Eh, EC and pH of discharged water were measured and its heavy metal concentrations were analyzed on ICP/MS.

(a) Dried contaminated and un-contaminated soil at 35℃

(b) Soil amendments (CaO, $CaCO_3$, Lime, Apatite and Limestone)



(c) Photograph of the column experiment.

(1: Contaminated soil without capping, 2: Capping with un-contaminated soil without mixed amendment, 3: Capping with 2wt% lime powder, 4: Capping with 5wt% lime powder, 5: Capping with 2wt% limestone powder, 6: Capping with 5wt% limestone powder, 7: Capping with 2wt% apatite powder, 8: Capping with 5wt% apatite powder, 9: Capping with 5wt% granular lime and 10: Capping with 5wt% granular limestone)

Fig. 6. Pilot scale column experiment for the capping treatment.

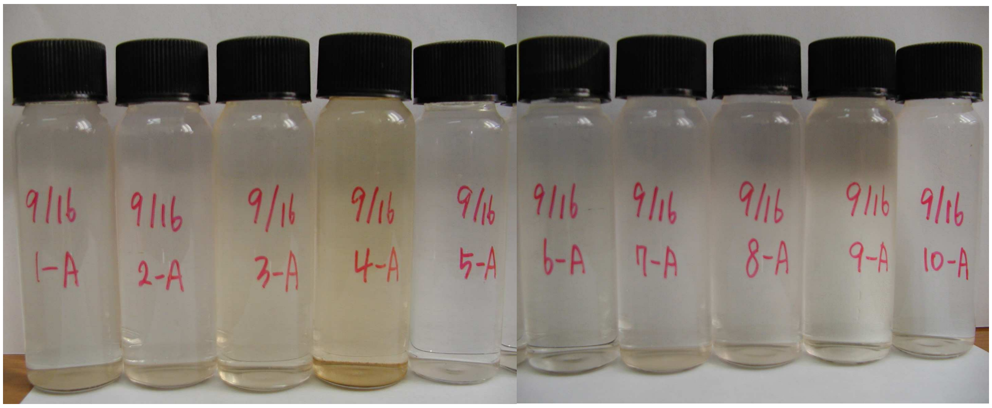


Fig. 7. Photograph of drain water from bottom of each column.

4.6 Evaluation for the leaching rate of contaminated soil with lime mixing treatment in pilot scale column experiments

Capping soil treatment needs clean soil to cover contaminated soils, but the mixing treatment needs only the mixing process of contaminated soil with amendments. Therefore, the cost of the "mixing treatment" was cheaper than that of the "caping treatment". Like the capping treatment, an acryl column (18.9 in diameter and 30cm in height), which of the upper and lower part consist of dense lattice screen plates and the drain system for injection and extraction of artificial rainfall, was used for the mixing treatment.

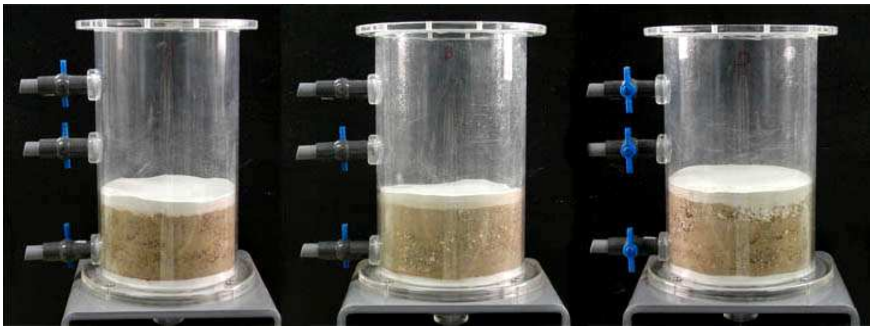
The average amount of rainfall per month around Goro mine was 91.2mm, which was determined as artificial rainfall, but only one-third of rainfall was considered to flow down into soil medium, which was sprayed on the column everyday. One day of the column experiment represented to one month duration in the field condition.

Contaminated soil of 27kg was dried at 35℃. Lime amendment was granulated (4.75~2.00mm in diameter) for the experiment. Each column was packed with Ottawa sand (1cm in thickness) at the bottom of column and then contaminated soils, which was mixed with granulated lime, was packed on the top of the Ottawa sand (in 10 cm thickness).

At every 12hr, 817.15ml of artificial rain was sprayed on the top of the column and discharged water was sampled from the bottom of the column. Eh, EC and pH of discharged water (treated water) were measured and its heavy metal concentrations analyzed on ICP/MS (Perkin Elmer, Elan 6100). Top of the column was packed with Ottawa sand of 2cm in thickness. Table 3. shows conditions of the mixing treatment and Fig. 8 shows the column experiment for the mixing treatments.

Table 3. The amount of contaminated soil, amendment for mixing experiment

For contaminated soil	Area of column	268.8cm^2
	Column thickness of contaminated soil	10cm
	Soil wet bulk density	1.38kg/m^3
	Total amount of contaminated soil	**3.76kg**
For amendment	5wt% of granulated lime	**198g**
	10wt% of granulated lime	**418g**


(a) (b) (c)

(a) : Contaminated soil without lime mixing treatment

(b) : Contaminated soil mixed with 5wt% lime

(c) : Contaminated soil mixed with 10wt% lime

Fig. 8. Pilot scale column experiment with the mixing treatment.

CHAPTER 5. RESULT & DISCUSSION

5.1 Arsenic and other heavy metal concentrations of soil around Goro abandoned mine

Heavy metal concentrations of soil sampled from nearby Goro abandoned mine for the experiment were shown in Table 4. Uncontaminated soil, which was not under the influence of Goro mine activity was also collected for the experiment. As concentration of contaminated soil was 198.15 mg/kg, which was higher than 33 times of Korea Soil Pollution Warning Limit (KSPWL : 6.0 mg/kg). Cd, Pb and Zn concentration were also higher than KSPWL. Contaminated soils used in experiments contained various heavy metals and then, need the pertinent remediation process.

The pH of contaminated soil and un-contaminated soil for the capping treatment were also measured and they turned out the week acid between pH 5.16 to 5.25 (Table 4). Results of the principle component analysis for contaminated soil and uncontaminated soil were shown in Table 5. The textural property of the soil, called textural class was determined on the basis of the mass ratios of three fractions. Contaminated soil is composed of 39% sand, 60% silt, and 0.4% clay. More than 99% of soil particle fell under "sand" and "silt" size range by the grain size distribution analysis (Fig. 9).

Table 4. Heavy metal concentration and pH of contaminated soil and capping (uncontaminated) soil

(mg/kg)	As	Cd	Pb	Zn	pH
Contaminated soil	*198.15*	*8.36*	*790.90*	*486.87*	5.25
Uncontaminated soil	0.00	0.00	2.85	1.33	5.16
KSPWL	6.00	1.50	100.00	300.00	-

* KSPWL : Korea Soil Pollution Warning Limit

Table 5. Result of principle component analysis for contaminated soil by XRF

Main Components	Mass distribution ratio (wt%)	
	Contaminated soil	uncontaminated soil
SiO_2	66.48	66.38
Al_2O_3	17.61	15.68
Fe_2O_3	5.34	4.84
K_2O	2.79	2.48
MgO	1.65	1.93
Na_2O	1.28	1.08
CaO	1.17	6.04
ZnO	0.84	0.03
TiO_2	0.63	0.84
MnO	0.43	0.15
SO_3	0.41	0.30
P_2O_5	0.16	0.20
ZrO_2	0.03	0.01
Total	98.82	99.96

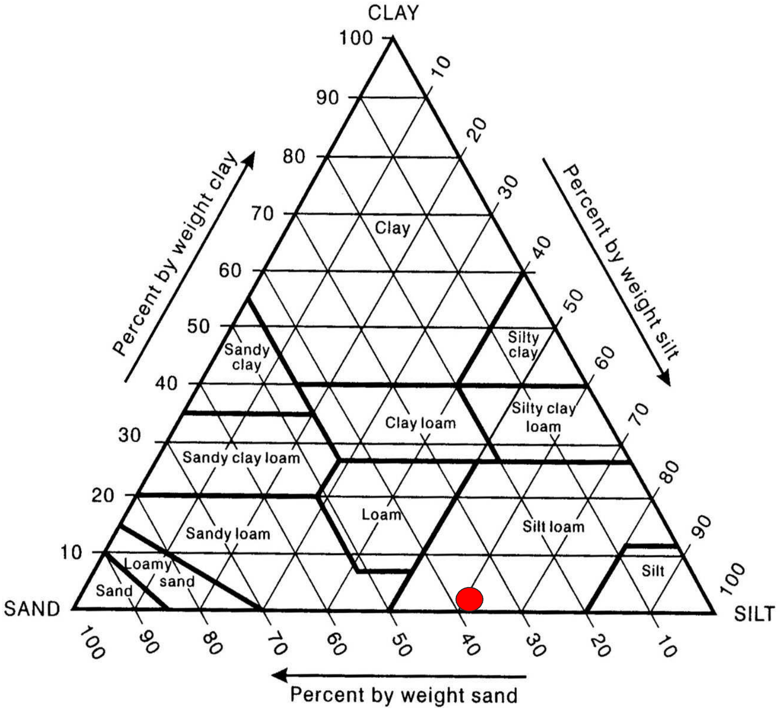


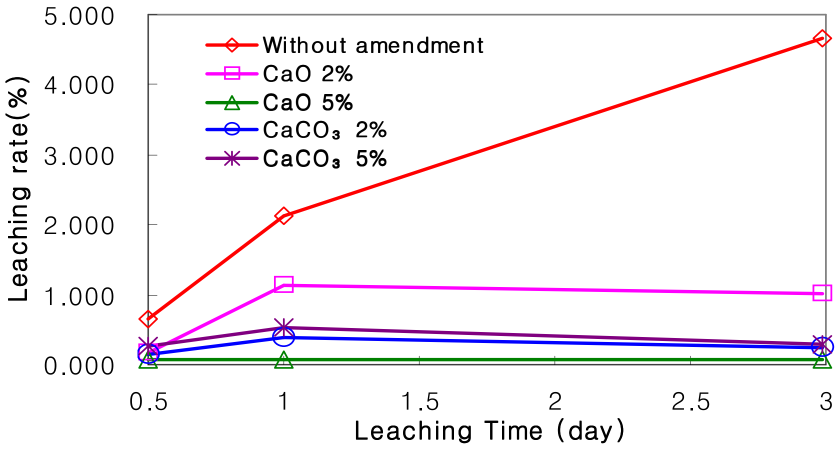
Fig 9. Result of soil textural for contaminated soil by grain size analysis (● : textural domain of contaminated soil).

5.2 Verification of decreased leaching rate by using soil amendments through batch experiment

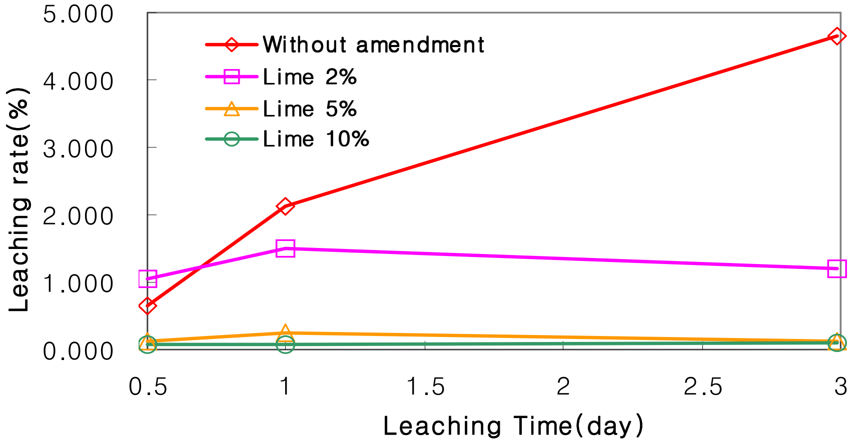
Five amendments were used to investigate the leaching rate decrease in batch experiments. Leaching rates of As, Cd, Pb, and Zn were calculated on the basis of initial soil heavy metals solution extracted with Korean Soil Analysis Method. Adding of soil amendments, leaching rate of heavy metals was stabilized within one day and thus 3 day was decided to the maximum shaking time for batch experiments.

Result of As

By using CaO (2wt%) and $CaCO_3$ (2wt%), As leaching rate decreased 4 times and 20 times, compared with that of contaminated soil without of amendments. With 5 wt% of CaO and $CaCO_3$, As leaching rate decreased to 74 times and 15 times (Fig. 10). With the addition of 2 wt% of lime, the leaching rate of As reduced 4 times and decreased 74 times and 15 times with 5 wt% and 10 wt% of lime (Fig. 10). While 2 wt%, 5 wt% and 10 wt% of limestone was added, As leaching rate reduced 11 times, 17 times and 13 times, respectively (Fig. 11). Apatite showed the lowest stability efficiency, decreasing the leaching rate only two times with 2-10 wt% of apatite (Fig. 11). Except apatite, four amendments lowered leaching rate more than 20 times (50 times in maximum), compared with that of soils without amendment, suggesting that these amendments are very useful to prevent As extraction from contaminated soils.

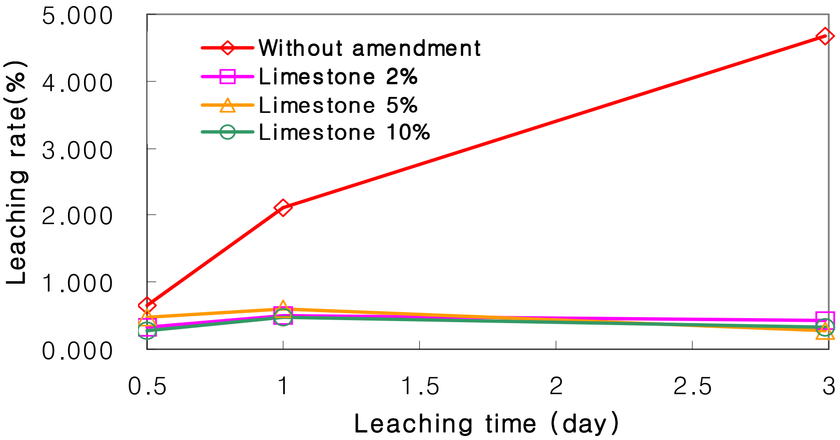


(a) As leaching rate decrease with CaO and $CaCO_3$ addition

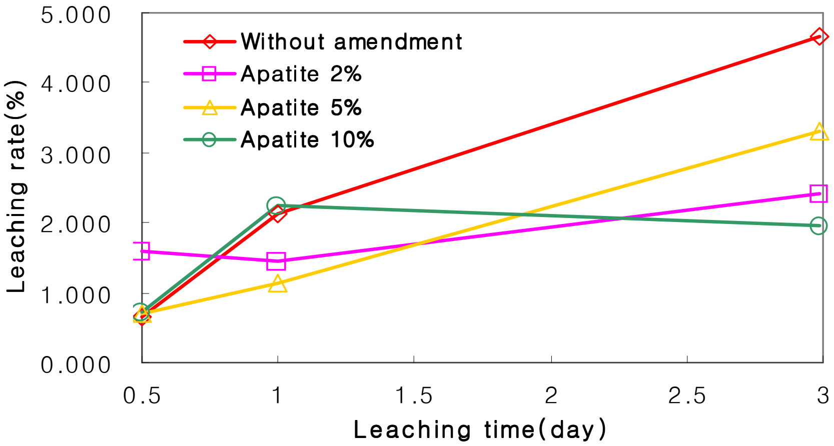


(b) As leaching rate decrease with lime addition

Fig. 10. Results of batch experiment for As leaching rate with CaO, $CaCO_3$ and lime addition.



(a) As leaching rate decrease with limestone addition



(b) As leaching rate decrease with apatite addition

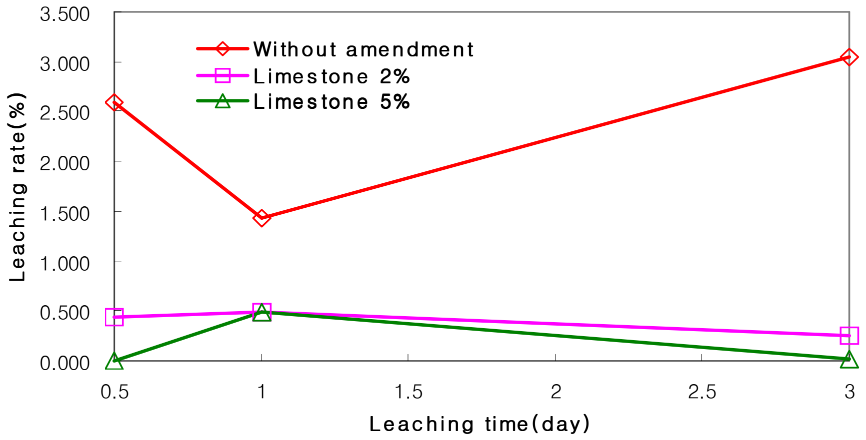
Fig. 11. Results of batch experiment for As leaching rate with limestone and apatite addition.

Result of Cd, Pb and Zn

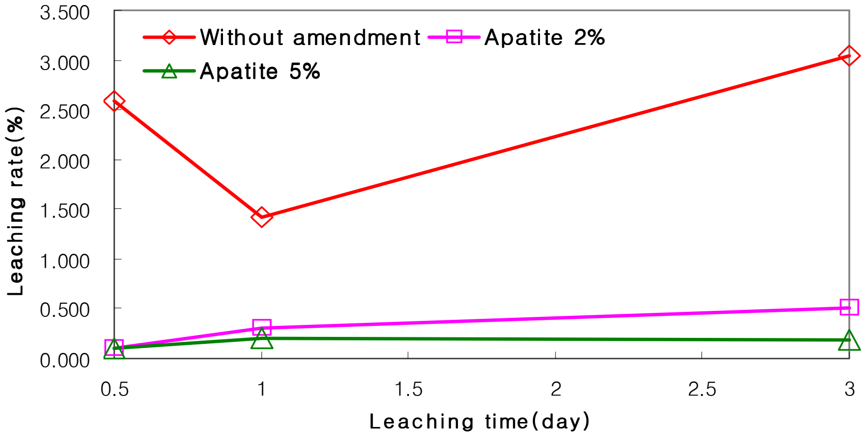
The decreasing pattern of Cd leaching rate was similar to that of As in batch experiments. The concentration of Cd in extracted solution without amendment was 12 ppb and Cd leaching rate from contaminated soil ranged from 1.5 % to 3.0 % (Fig. 12). With limestone and apatite, Cd concentrations of solution was between 1.27 ppb and 0.105 ppb, and the leaching rate reduced to one-seventeenth for 3 day. With CaO (5 wt%) and $CaCO_3$ (5 wt%), Cd leaching rate dramatically decreased to 0.06% for 3 day (50-126 times lower than the initial concentration of solution without amendment) (Fig. 13). While 5 wt% of lime was added, Cd concentration dropped down to 0.355 ppb and the leaching rate decreased 0.02 % within one day, suggesting that lime was very effective to stabilize Cd from contaminated soils (Fig. 13).

For five of amendments, Pb leaching rate dropped down to 0.02% and Pb concentration of solution was 630 times lower than that of solution without amendment (Fig. 14 and Fig. 15). Results suggesting that Pb could be easily stabilized by using any kind of amendments used in experiments.

Concentration of Zn in solution without amendment was 1.353 ppm and Zn leaching rate was 4~5 % compared with Zn concentration of soil (Fig. 16). By adding lime and limestone (2 wt%), Zn leaching rate reduced 150 times, compared with that of solution without amendment (Fig. 17). Most of Zn were stabilized with the addition of any kind of amendments used in experiments.

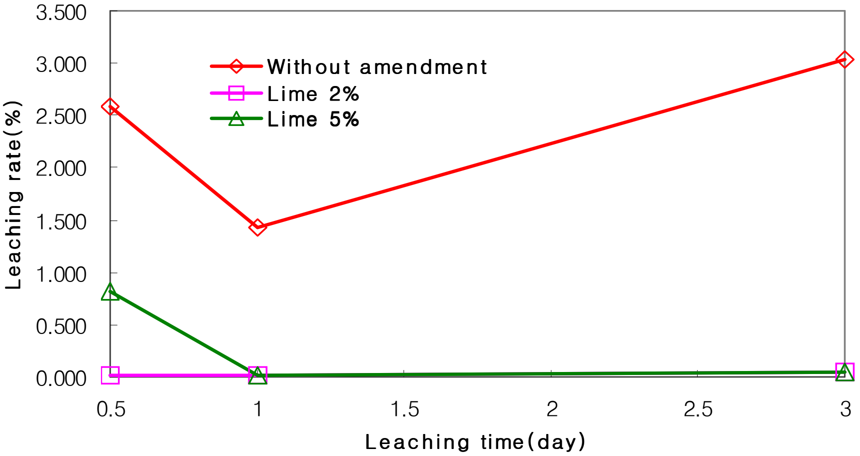


(a) Cd leaching rate decrease with limestone addition

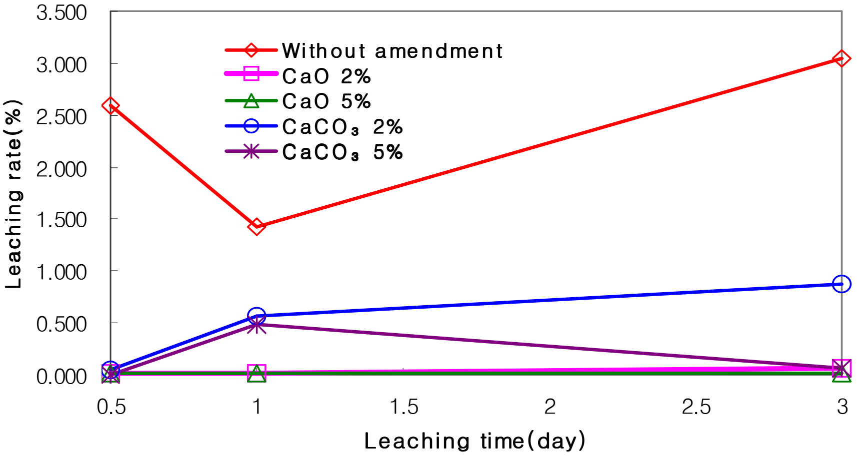


(b) Cd leaching rate decrease with apatite addition

Fig. 12. Results of batch experiment for Cd leaching rate with limestone and apatite addition.

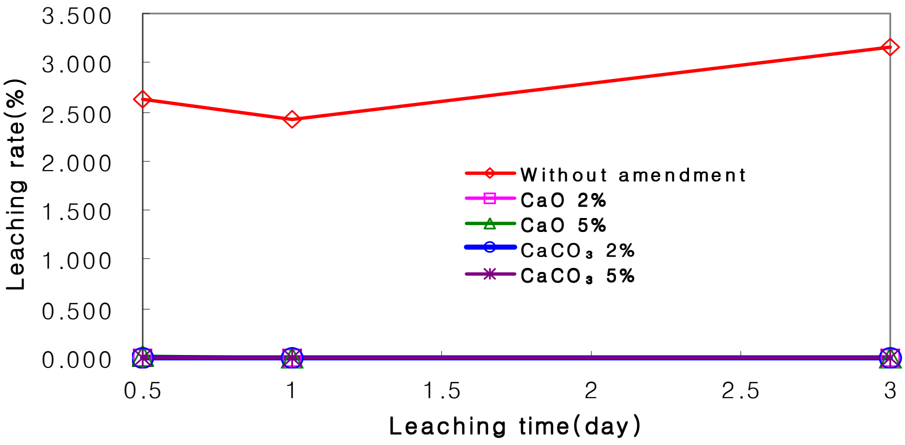


(a) Cd leaching rate decrease with lime addition

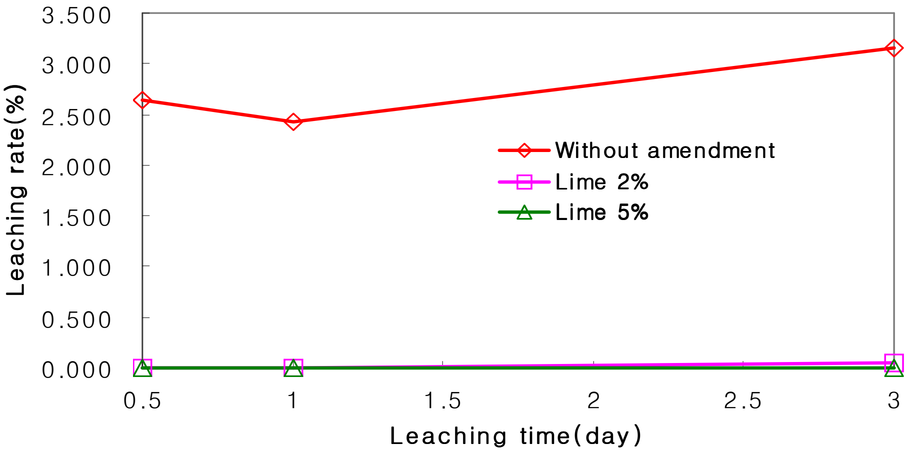


(b) Cd leaching rate decrease with CaO and $CaCO_3$ addition

Fig. 13. Results of batch experiment for Cd leaching rate with lime, CaO and $CaCO_3$ addition.

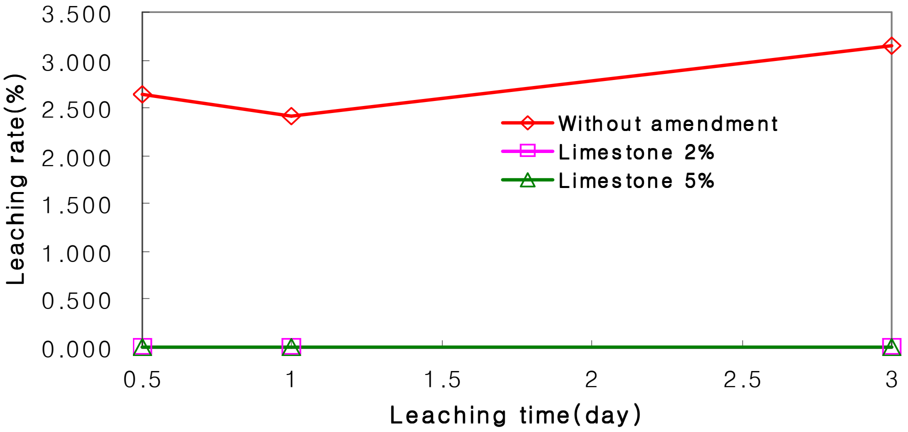


(a) Pb leaching rate decrease with CaO and $CaCO_3$ addition

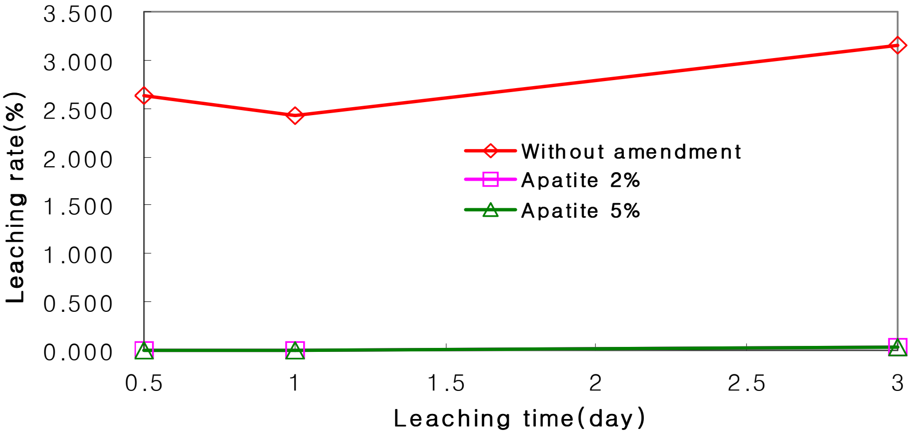


(b) Pb leaching rate decrease with lime addition

Fig. 14. Results of batch experiment for Pb leaching rate with CaO, $CaCO_3$ and lime addition.

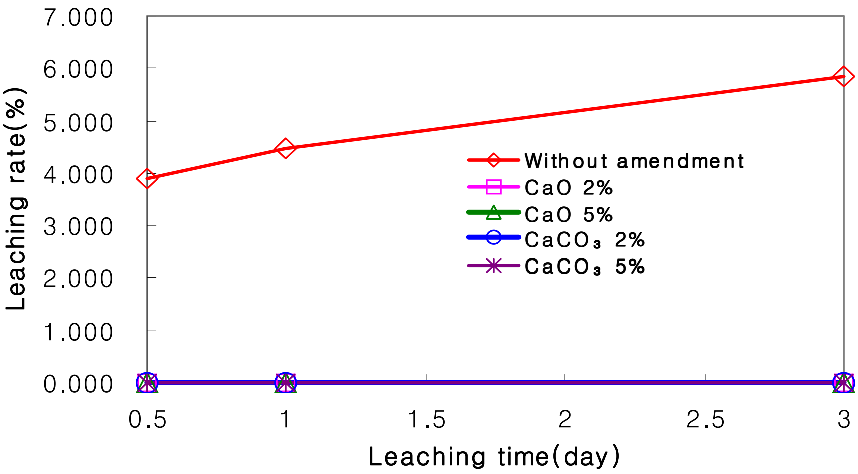


(a) Pb leaching rate decrease with limestone addition

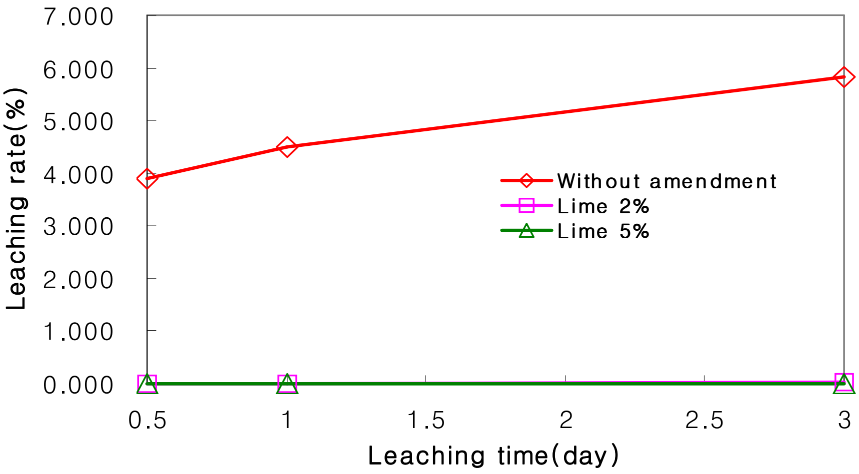


(b) Pb leaching rate decrease with apatite addition

Fig. 15. Results of batch experiment for Pb leaching rate with limestone and apatite addition.

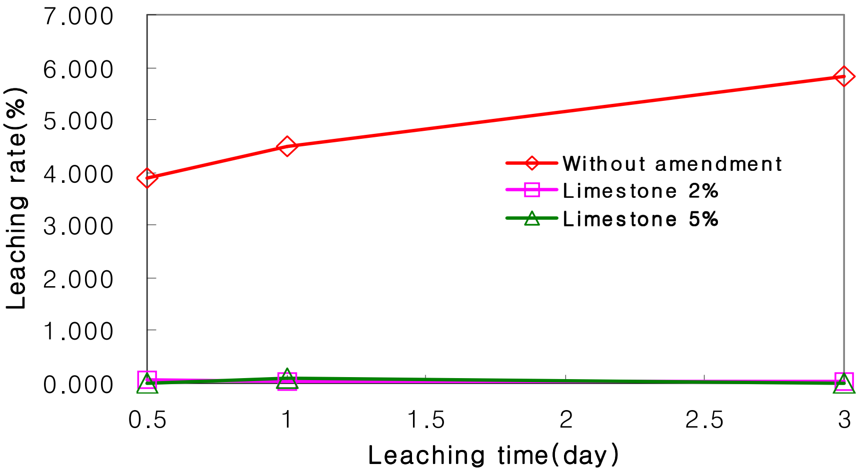


(a) Zn leaching rate decrease with CaO and $CaCO_3$ addition

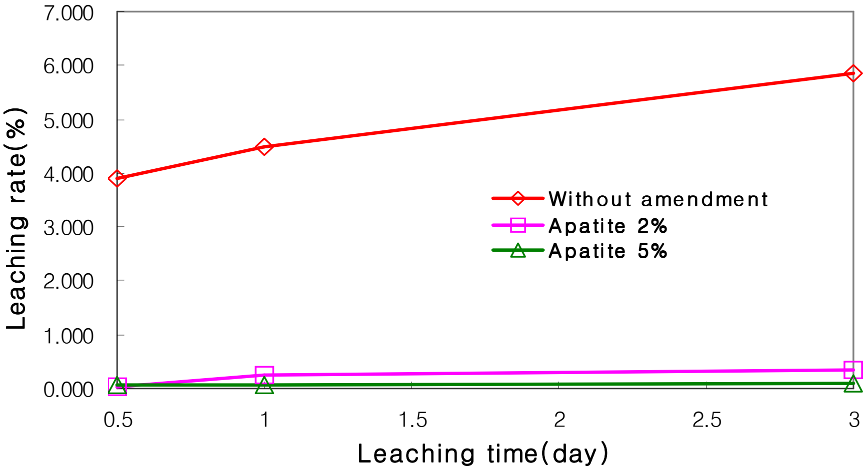


(b) Zn leaching rate decrease with lime addition

Fig. 16. Results of batch experiment for Zn leaching rate with CaO, $CaCO_3$ and lime addition.



(a) Zn leaching rate decrease with limestone addition



(b) Zn leaching rate decrease with apatite addition

Fig. 17. Results of batch experiment for Zn leaching rate with limestone and apatite addition.

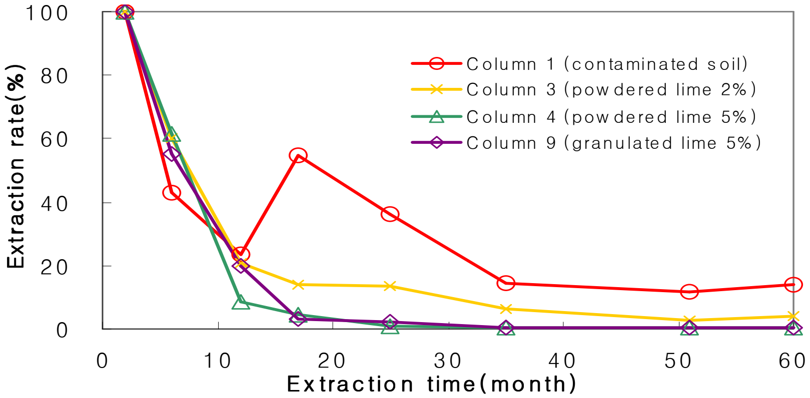
5.3 Results of "the capping treatment" of pilot scale column experiment

Pilot scale column experiments were performed to investigate the stabilization of heavy metals in contaminated soil, and powdered or granulated (2-4mm in diameter) amendments such as CaO, $CaCO_3$, lime, limestone and apatite were used. Packing properties of columns and heavy metal concentrations of column soils may be different and thus, the leaching rate was calculated based on the heavy metal concentration of the frist water sample drained from the column without amendments.

Result of Cd extraction in column experiment

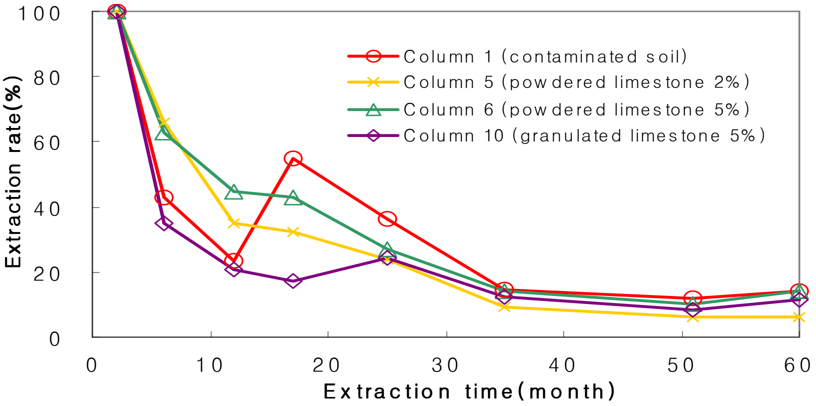
Without capping treatment, Cd concentration of extracted water from the column maintained about 70 ppb for 5 years, and its value was much higher than the groundwater tolerance limit (10 ppb). In the column applying to the capping treatment with 2 wt% powdered lime, Cd concentration of drained water reduced down to 5 ppb, and with 5 wt% of powdered lime, Cd concentration was lower than 0.7 ppb (100 times lower than the concentration without amendment) (Fig. 18(a)). Results of extraction rate with granulated lime were very similar to those of powdered lime treatment, suggesting that the use of granulated lime was enough for the capping treatment to stabilize Cd in contaminated soils.

In the capping treatment with 2wt% of powdered or granulated limestone, Cd concentration of drained water from the column decreased to 20 ppb, which was higher than the groundwater tolerance limit (10 ppb) (Fig. 18(b)). Results of apatite treatment was similar to those of limestone treatment, which of Cd extraction rate was ten times higher than that of lime treatment (Fig. 18(c)). From column experiments, the capping treatment with 5 wt% of lime was considered to be the most effective to decrease Cd concentration from contaminated soils.

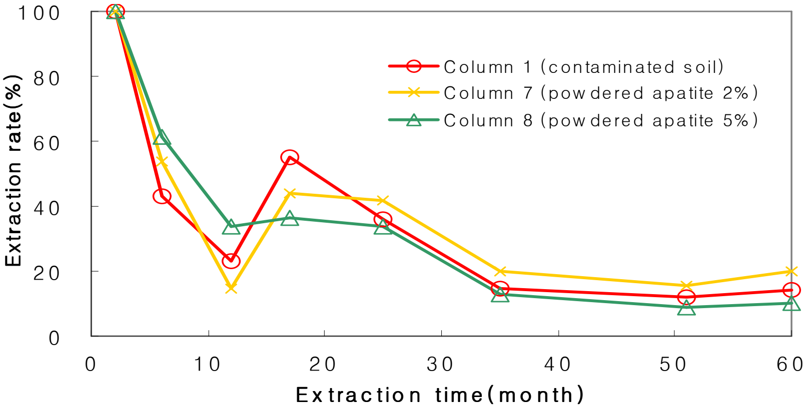


(a) Cd extraction rate decrease with lime addition

Fig. 18. Results of Cd extraction rate in the capping treatment.



(b) Cd extraction rate decrease with limestone addition

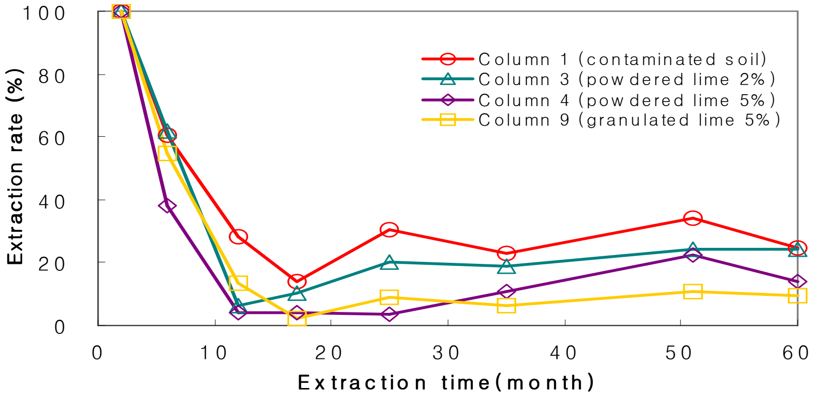


(c) Cd extraction rate decrease with apatite addition

Fig. 18. Results of Cd extraction rate in the capping treatment (continued).

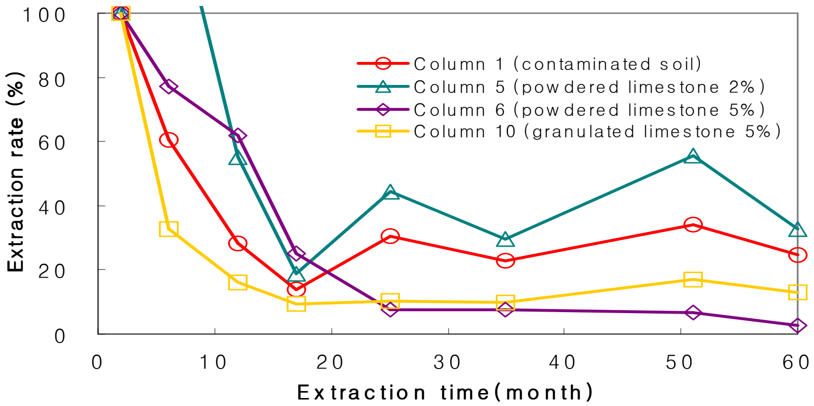
Result of Pb extraction in column experiment

Pb concentration of drained water from the column, which was not applied by the capping treatment, maintained about 60 ppb. With the treatment of 5 wt% lime, Pb concentration of drained water decreased to 30 ppb, which was 2 times lower compared with the initial concentration of drained water in the column (Fig. 19(a)). Because considerable diminish of Pb extraction from soils occurred in the column without the capping treatment, Pb extraction rate difference between the column with limestone (apatite) treatment and the column without the capping treatment was negligible (Fig. 19(b) and (c)). From column experiments, 5 wt% of lime capping treatment was shown as the most available amount applying to decrease the leaching rate of Pb.

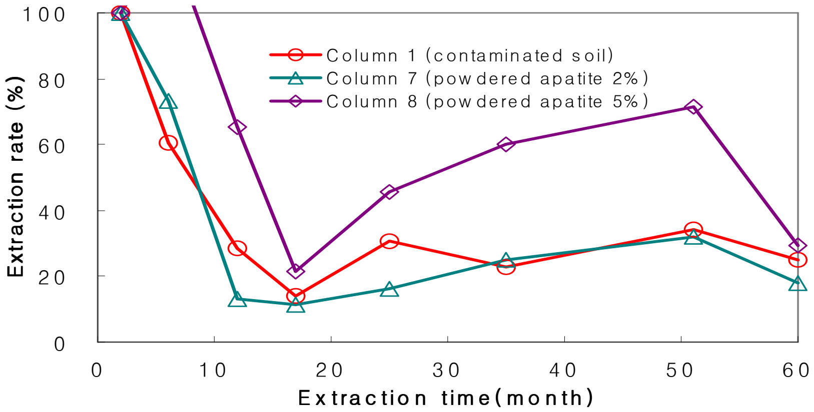


(a) Pb extraction rate decrease with lime addition

Fig. 19. Results of Pb extraction rate in the capping treatment.



(b) Pb extraction rate decrease with limestone addition



(c) Pb extraction rate decrease with apatite addition

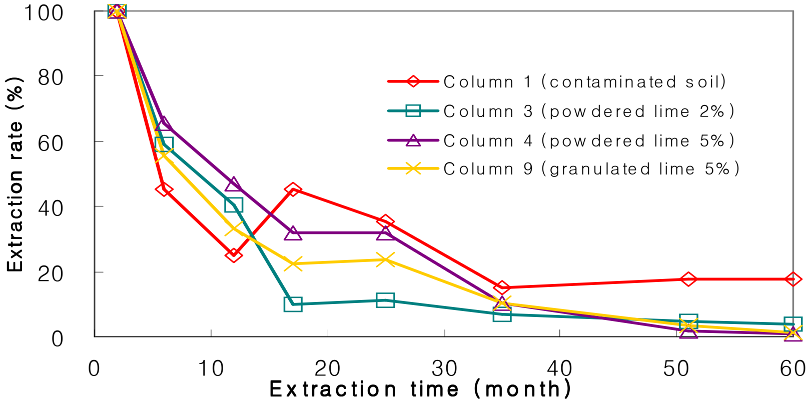
Fig. 19. Results of Pb extraction rate in the capping treatment (continued).

Result of Zn extraction in column experiment

Zn concentration of drained water from the column decreased about one-tenth with lime or limestone treatment (5 wt%), and its concentration maintained 50 ppb after 3 year extraction (Fig. 20(a) and (b)).

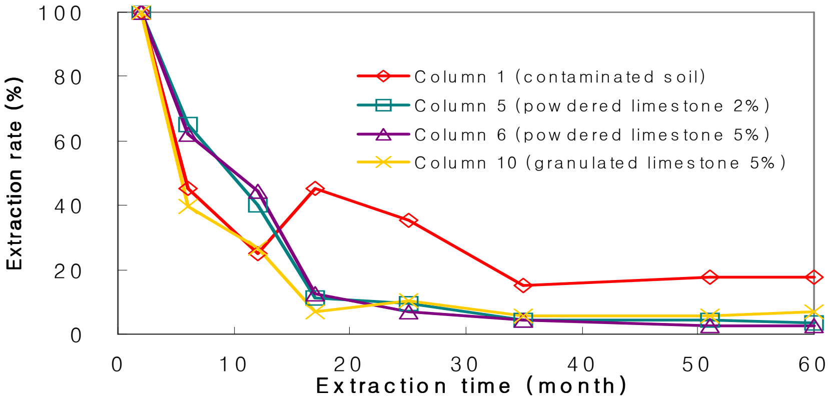
For the apatite treatment, Zn concentration decreased to about 1000ppb, and the extraction rate was 10-15 % during 5 year extraction (Fig. 20(c)).

From pilot scale column experiments, 2-5 wt% of lime for the capping treatment was shown to be the most available to decrease heavy metal extraction from contaminated soils.

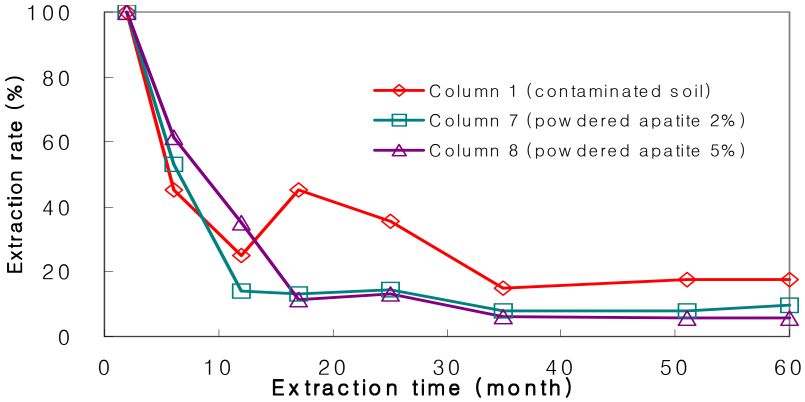


(a) Zn extraction rate decrease with lime addition

Fig. 20. Results of Zn extraction rate in the capping treatment.



(b) Zn extraction rate decrease with limestone addition



(c) Zn extraction rate decrease with apatite addition

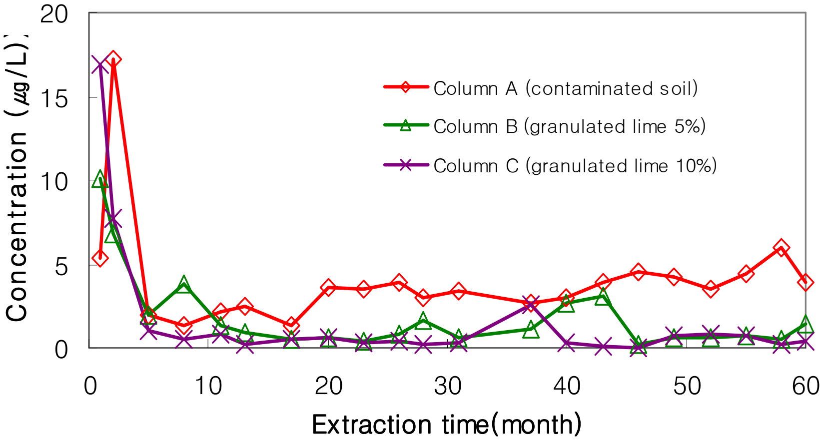
Fig. 20. Results of Zn extraction rate in the capping treatment (continued).

5.4 Results of "the mixing treatment" of pilot scale column experiment

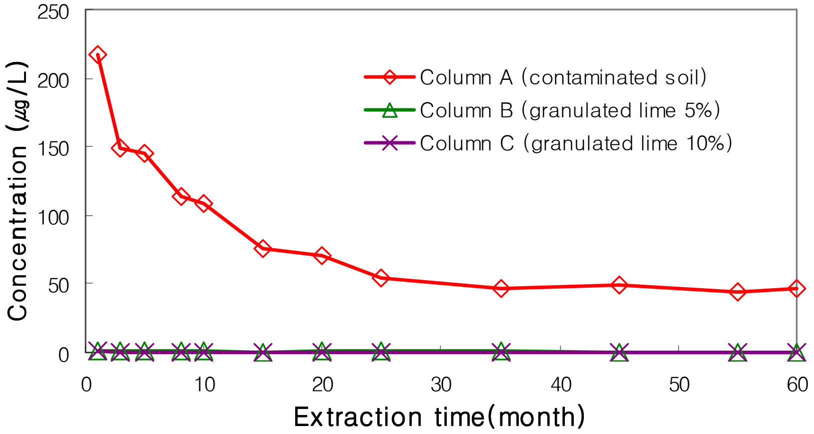
From results of the capping treatment, it was suggested that granulated lime have a great capability to stabilize heavy metals from the soil. For the pilot scale column experiments with the mixing treatment, granulated lime and contaminated soils at Goro mine were mixed at 1:20 and 1:10 ratio (5 wt% and 10 wt%).

The initial As concentration of drained water with 5 wt% of lime mixing was 10 ppb and it decreased to less than 0.5 ppb after 1 year extraction (Fig. 21,(a)). For 10 wt% of lime mixing treatment, As concentration of drained water immediately reduced down to 0.2 ppb few months later. However, As concentration in the column without the mixing treatment, maintained about 5.0 ppb after one year extraction.

Cd concentration in the column without the mixing treatment maintained about 50 ppb (five times higher than groundwater tolerance limit) after 2 year extraction, however, with 5 wt% of lime mixing treatment, Cd concentration reduced from 220 ppb to 1.2 ppb (Fig. 21,(b)). With lime mixing treatment, Zn concentration maintained less than 4000 ppb after few month extraction, which was 400 times lower than the initial concentration (Fig. 21(c)). Results investigated that the stabilization efficiency for heavy metals in the mixing treatment was higher than that in the capping treatment.

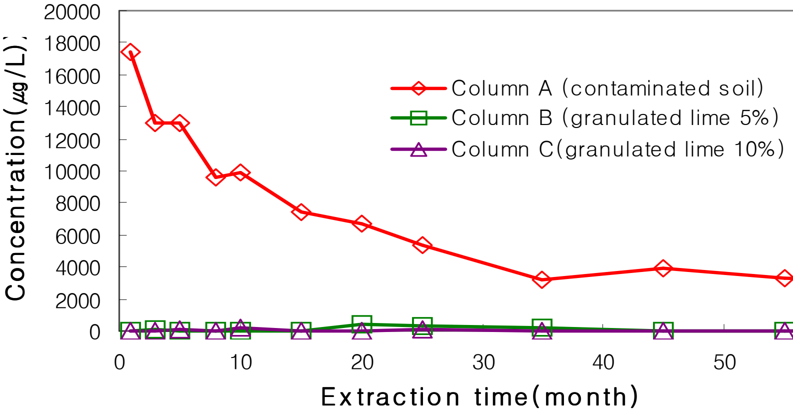


(a) As extraction decrease from the column with the mixing treatment.



(b) Cd extraction decrease from the column with the mixing treatment.

Fig. 21. Results of the pilot scale column experiment with the lime mixing treatment.



(a) Zn extraction decrease from the column with the mixing treatment

Fig. 21. Results of the pilot scale column experiment with the lime mixing treatment (continued).

CHAPTER 6. CONCLUSION

The capability of amendments such as lime, limestone and apatite to decrease extraction of heavy metals from contaminated soils, were investigated by batch and pilot scale column experiments. Following conclusions were derived from the study.

1. Soil amendments such as lime, limestone and apatite decreased the leaching rate of As, Cd, Pb and Zn from contaminated soil. Especially, the addition of lime was very effective to decrease the leaching rate of As and other heavy metals. With the addition of 2 wt% of lime, the leaching rate of As reduced 4 times and decreased 74 times and 15 times with 5 wt% and 10 wt% of lime. For five of amendments, Pb leaching rate dropped down to 0.02% and Pb concentration of solution was 630 times lower than that of solution without amendment. By adding lime and limestone (2 wt%), Zn leaching rate reduced 150 times compared with that of solution without amendment.

2. "Capping soil treatment" process by using lime dramatically decreased the extraction of heavy metals from contaminated soil. In case of adding lime (5 wt%), Cd extraction rate reduced more than 157 times, compared with initial extraction rate. With 2 wt% of powdered lime, Cd concentration in drain water dropped down to 5 ppb, and with 5 wt% of powdered lime, Cd concentration was lower than 0.7ppb (100 times lower than the concentration without

amendment). With the treatment of 5 wt% lime, Pb concentration of drain water decreased to 30ppb, which was 2 times lower compared with the initial concentration of drain water in the column. Zn concentration of drain water from the column decreased about one-tenth with lime or limestone treatment (5 wt%), and its concentration maintained 50ppb after 3 year extraction.

3. "Mixing soil treatment" process by using lime had a great efficiency to decrease As, Cd and Zn extraction rate from contaminated soil. For 5 wt% of lime mixing, As concentration decreased to less than 0.5 ppb after 1 year extraction. Cd and Zn concentration decreased 200-400 times with 10 wt% granular lime mixing treatment in few months.

4. The efficiency of stabilization for heavy metals with "Mixing soil treatment" was higher than that with "Capping soil treatment". Because of its low cost, high efficiency, and easy operation, the lime treatment as a stabilization process will become one of major processes to control heavy metal contaminated soil.

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토양 개량제를 이용한 폐광산 주변 비소 및 중금속 오염토양의 안정화 공법의 적용

이 예 선

부경대학교 대학원 응용지질학과

대부분의 폐광산 주변지역은 광산으로부터 발생한 광미, 광폐석 등에 의하여 비소 및 각종 중금속으로 오염되어 있으며, 이러한 중금속들의 지속적인 용출에 의해 주변 지하수/토양 오염과 재배 농산물의 중금속 축적이 우려되고 있다. 오염토양으로부터 중금속 용출에 의한 오염을 막기 위하여, 본 연구에서는 개량제를 이용한 토양 안정화 공법을 선택하여 토양층 하부로 이동하는 중금속의 용출율을 감소시키는 배치 및 칼럼 실험을 실시하였다.

실험에 사용한 토양은 경북 군위군에 위치한 고로 폐아연 광산 지역의 토양이며, 실험에 사용한 개량제는 총 5가지로서 시약용 ACS grade인 CaO와 $CaCO_3$, 그리고 비료용으로 사용하는 생석회(lime), 석회암 원석을 분쇄한 석회석(limestone), 중국산 인회석(apatite)을 사용하였다. 개량제의 중금속 용출율 감소 효율을 알아보기 위한 배치실험을 실시하였으며, 개량제의 함량을 0, 2, 5, 10wt%로 다양하게 사용하였다. 개량제를 첨가하여 실시한 배치실험 결과, 용출율은 만 하루가 지난 후 대부분 안정화 되었으므로 배치실험에서의 최대 용출시간을 3일로 하였다. 배치실험 결과 인회석을 제외한 나머지 4개의 개량제들을 첨가한 경우, 비소의 용출율 감소가 약 20배 이상, 최대 50배 정도 나타나 비소의 용출율 감소에 이러한 개량제들이 큰 효과를 나타내었다. 또한 카드뮴과 납, 아연의 용출율 감소도 비소의

용출율 감소 효과와 비슷하게 나타나 이러한 개량제들의 중금속 용출율 감소 효과가 매우 큰 것으로 나타났다.

배치실험 결과들을 바탕으로 하여 현장 적용 가능성을 평가해보기 위한 대형 칼럼 실험을 실시하였다. 안정화 공법의 대표적인 공정인, '복토법'과 '객토법'을 선정하여 칼럼실험을 실시하였다. 복토법의 경우, 앞서 사용한 비료용 생석회와 석회석, 인회석을 분말과 입상으로 나누어 사용하되, 오염되지 않은 토양을 각각의 안정화제들과 혼합하여 오염된 토양 위에 복토하였다. 각각의 칼럼 상부로부터 인공 강우를 주입하여 칼럼 스케일로 최대 5년 동안의 용출율을 분석하였다. 분말 생석회와 입상 생석회를 사용한 결과 용출율의 차이는 거의 없는 것으로 나타났으며, 5wt%의 생석회를 투입한 결과 카드뮴의 용출율이 약 157배 정도 감소하는 것으로 나타났다. 반면 석회석과 인회석을 사용한 결과는 생석회로 복토한 결과에 비교하여 볼 때 낮은 용출율 감소 효율을 보였다.

객토법은 오염된 토양과 각각의 개량제를 직접 오염토양에 적용, 혼합하여 실험을 실시하였다. 앞서 실시한 복토법에서 효율이 높았던 입상 생석회를 사용하여 객토를 실시한 결과 매우 높은 비소 및 카드뮴, 납의 용출율 감소 효율을 보였다. 5wt%의 생석회를 적용한 칼럼에서 1년이 지난 후 비소의 용출농도가 10ppb에서 0.5ppb로 감소하였으며, 10wt%의 생석회를 적용한 칼럼에서 몇 개월 이내에 카드뮴과 아연의 용출농도가 약 200~400배 정도 감소하였다.

배치 및 칼럼실험 결과로부터, 객토법이 복토법에 비해 더 좋은 안정화 효율을 보여주었으며, 생석회가 여러 개량제들 가운데 가장 높은 중금속 용출율 감소 효과를 나타내었다. 본 연구에서 도출한 결과로 부터 중금속 오염토양의 복원에 생석회를 이용한 토양 안정화 공법이 효과적으로 사용될 수 있을 것으로 판단된다.

주제어 : 비소, 안정화공법, 생석회, 토양 복원, 폐광산, 중금속 오염

APPENDIX

TABLE & PUBLICATIONS

Table 1. The results of batch experiment for reducing leaching rate from contaminated soil (As)

	Time (day)	Concentration (mg/kg)	Leaching rate (%)	pH in extraction solution	Eh in extraction solution	EC in extraction solution
Contaminated soil	0.5	0.207	**0.647**	6.1	8.7	6.98
	1	0.677	**2.117**	126.9	162.3	180.1
	3	1.491	**4.662**	19.57㎳	18.84㎳	19.43㎲
CaO 2%	0.5	0.055	**0.172**	11.2	11.3	10.99
	1	0.366	**1.144**	109.6	136	91.3
	3	0.328	**1.026**	736㎲	1020㎲	433㎲
CaO 5%	0.5	0.023	**0.072**	11.2	12	11.52
	1	0.024	**0.075**	110.5	119.5	81.9
	3	0.02	**0.063**	3.55㎳	3.56㎳	3.60㎳
Lime 2%	0.5	0.334	**1.044**	10.9	10.5	10.09
	1	0.479	**1.498**	144.3	96.7	116.9
	3	0.384	**1.201**	266.9㎲	244.7㎲	105.4㎲
Lime 5%	0.5	0.043	**0.134**	11.2	11.6	11.84
	1	0.082	**0.256**	131	98.7	139.1
	3	0.038	**0.119**	1800	1951㎲	1353㎲
Lime10%	0.5	0.020	**0.063**	12.0	12.0	12.13
	1	0.024	**0.075**	129.7	141.6	53.1
	3	0.03	**0.094**	4.12㎳	4.63㎳	5.55㎳
Apatite 2%	0.5	0.509	**1.591**	8.7	8.8	7.23
	1	0.460	**1.438**	203.7	164.4	331.3
	3	0.772	**2.414**	34.6㎲	39.7㎲	32.2㎲
Apatite 5%	0.5	0.224	**0.700**	8.7	8.7	7.12
	1	0.363	**1.135**	198.7	182.6	135.8
	3	1.062	**3.320**	34.8㎲	45.4㎲	51.7㎲
Apatite 10%	0.5	0.228	**0.713**	8.7	8.6	7.55
	1	0.716	**2.239**	211.7	194.8	84.9
	3	0.626	**1.957**	35.7㎲	43.1㎲	75.1㎲
$CaCO_3$ 2%	0.5	0.049	**0.153**	8.3	8.6	7.92
	1	0.123	**0.385**	213	147.7	134.2
	3	0.075	**0.234**	180.3㎲	213.5㎲	230.3㎲
$CaCO_3$ 5%	0.5	0.087	**0.272**	8.4	8.4	7.90
	1	0.169	**0.528**	200.7	180.2	145.0
	3	0.096	**0.300**	175.4㎲	200㎲	245.5㎲
Limestone 2%	0.5	0.105	**0.328**	8.2	8.3	8.06
	1	0.161	**0.503**	208.5	192.1	111.9
	3	0.135	**0.422**	144.3㎲	208.9㎲	222.4㎲
Limestone 5%	0.5	0.15	**0.469**	8.2	9.0	7.97
	1	0.192	**0.600**	223.7	198.6	135.7
	3	0.087	**0.272**	184.1㎲	210.0㎲	240.7㎲
Limestone10%	0.5	0.087	**0.272**	8.2	8.4	7.96
	1	0.151	**0.472**	214.3	211.8	145.5
	3	0.108	**0.338**	180.7㎲	211.5㎲	259.5㎲

Table 2. The results of batch experiment for reducing leaching rate from contaminated soil (Cd, Pb, Zn)

	Time (day)	Cd		Pb		Zn	
		Cd (mg/kg)	Leaching rate (%)	Pb (mg/kg)	Leaching late (%)	Zn (mg/kg)	Leaching rate (%)
Contaminated soil	0.5	0.216	2.585	20.833	2.634	18.984	3.899
	1	0.119	1.427	19.167	2.423	21.836	4.485
	3	0.254	3.042	24.938	3.153	28.429	5.839
CaO (2%)	0.5	0.002	0.024	0.002	0.000	0.01	0.002
	1	0.002	0.024	0.023	0.003	0.048	0.010
	3	0.006	0.072	0.012	0.002	0.027	0.006
CaO (5%)	0.5	0.001	0.012	0.133	0.017	0.071	0.015
	1	0.001	0.012	0.001	0.000	0.002	0.000
	3	0.002	0.024	0.037	0.005	0.01	0.002
Lime (2%)	0.5	0.001	0.012	0.001	0.000	0.006	0.001
	1	0.002	0.024	0.005	0.001	0.012	0.002
	3	0.004	0.048	0.359	0.045	0.166	0.034
Lime (5%)	0.5	0.069	0.826	0.001	0.000	0.000	0.000
	1	0.002	0.024	0.001	0.000	0.005	0.001
	3	0.005	0.060	0.001	0.000	0.019	0.004
$CaCO_3$ (2%)	0.5	0.004	0.048	0.005	0.001	0.072	0.015
	1	0.047	0.562	0.015	0.002	0.466	0.096
	3	0.073	0.874	0.038	0.005	0.870	0.179
$CaCO_3$ (5%)	0.5	0.000	0.000	0.001	0.000	0.008	0.002
	1	0.041	0.491	0.006	0.001	0.499	0.102
	3	0.005	0.060	0.014	0.002	0.073	0.015
Limestone (2%)	0.5	0.036	0.431	0.009	0.001	0.344	0.071
	1	0.041	0.491	0.015	0.002	0.106	0.022
	3	0.021	0.251	0.066	0.008	0.186	0.038
Limestone (5%)	0.5	0.000	0.000	0.001	0.000	0.010	0.002
	1	0.041	0.491	0.008	0.001	0.408	0.084
	3	0.001	0.012	0.015	0.002	0.047	0.010
Apatite (2%)	0.5	0.009	0.108	0.003	0.000	0.200	0.041
	1	0.026	0.311	0.042	0.005	1.229	0.252
	3	0.042	0.503	0.231	0.029	1.599	0.328
Apatite (5%)	0.5	0.009	0.108	0.024	0.003	0.229	0.047
	1	0.017	0.203	0.028	0.004	0.291	0.060
	3	0.015	0.180	0.215	0.027	0.396	0.081

Table 3. Results of the pilot scale column experiment with the capping soil treatment (Cd)

	Time (month)	Conc. (㎍/L)	Leaching rate(%)		Time (month)	Conc. (㎍/L)	Leaching rate(%)
Column 1 (without amendment)	2	74.824	100.000	Column 6 (Powdered limestone 5%)	2	146.402	100.000
	6	32.254	43.106		6	92.000	62.841
	12	17.458	23.332		12	65.495	44.736
	17	41.090	54.916		17	62.760	42.868
	25	27.019	36.110		25	39.772	27.166
	35	10.893	14.558		35	20.678	14.124
	51	8.960	11.975		51	14.930	10.198
	60	10.569	14.125		60	21.029	14.364
Column 2 (capping without amendment)	2	89.054	100.000	Column 7 (Powdered apatite 2%)	2	128.268	100.000
	6	42.732	47.984		6	69.016	53.806
	12	29.259	32.855		12	18.733	14.605
	17	44.415	49.874		17	56.166	43.788
	25	46.747	52.493		25	53.682	41.851
	35	21.607	24.263		35	25.908	20.198
	51	17.840	20.033		51	19.919	15.529
	60	-	-		60	25.669	20.012
Column 3 (Powdered lime 2%)	2	135.399	100.000	Column 8 (Powdered apatite 5%)	2	94.291	100.000
	6	81.231	59.994		6	57.885	61.390
	12	28.469	21.026		12	32.046	33.986
	17	19.023	14.050		17	34.196	36.266
	25	18.136	13.394		25	31.979	33.915
	35	8.879	6.558		35	11.968	12.693
	51	3.797	2.804		51	8.193	8.689
	60	5.472	4.041		60	9.699	10.286
Column 4 (Powdered lime 5%)	2	123.171	100.000	Column 9 (Granulated lime 5%)	2	173.617	100.000
	6	75.589	61.369		6	95.467	54.987
	12	10.583	8.592		12	34.238	19.720
	17	5.473	4.443		17	5.230	3.012
	25	1.249	1.014		25	3.796	2.186
	35	0.785	0.637		35	1.006	0.579
	51	0.594	0.482		51	0.842	0.485
	60	0.764	0.620		60	1.177	0.678
Column 5 (Powdered limestone 2%)	2	107.032	100.000	Column 10 (Granulated limestone 5%)	2	211.210	100.000
	6	70.333	65.712		6	73.469	34.785
	12	37.529	35.063		12	44.346	20.996
	17	34.790	32.504		17	36.370	17.220
	25	25.660	23.974		25	51.066	24.178
	35	9.833	9.187		35	25.825	12.227
	51	6.570	6.138		51	17.301	8.191
	60	6.437	6.014		60	23.988	11.357

Table 4. Results of the pilot scale column experiment with the capping soil treatment (Pb)

	Time (month)	Conc. (㎍/L)	Leaching rate(%)		Time (month)	Conc. (㎍/L)	Leaching rate(%)
Column 1 (without capping)	2	60.719	100.000	Column 6 (Powdered limestone 5%)	2	125.599	100.000
	6	36.694	60.432		6	96.723	77.009
	12	17.226	28.370		12	77.826	61.964
	17	8.573	14.119		17	31.492	25.073
	25	18.607	30.644		25	9.538	7.594
	35	13.877	22.854		35	9.416	7.497
	51	20.707	34.103		51	8.657	6.893
	60	15.07	24.819		60	3.497	2.784
Column 2 (capping without amendment)	2	76.250	100.000	Column 7 (Powdered apatite 2%)	2	149.041	100.000
	6	70.741	92.775		6	109.479	73.456
	12	29.560	38.767		12	19.313	12.958
	17	30.771	40.355		17	16.818	11.284
	25	23.670	31.043		25	24.080	16.157
	35	12.713	16.673		35	37.183	24.948
	51	42.401	55.608		51	47.735	32.028
	60	-	-		60	26.799	17.981
Column 3 (Powdered lime 2%)	2	323.186	100.000	Column 8 (Powdered apatite 5%)	2	29.868	100.000
	6	199.735	61.802		6	36.806	123.229
	12	20.667	6.395		12	19.557	65.478
	17	33.673	10.419		17	6.480	21.695
	25	65.612	20.302		25	13.688	45.828
	35	61.550	19.045		35	17.968	60.158
	51	77.658	24.029		51	21.352	71.488
	60	78.673	24.343		60	8.762	29.336
Column 4 (Powdered lime 5%)	2	273.323	100.000	Column 9 (Granulated lime 5%)	2	343.555	100.000
	6	104.201	38.124		6	187.764	54.653
	12	10.856	3.972		12	45.999	13.389
	17	10.547	3.859		17	7.693	2.239
	25	9.333	3.415		25	31.545	9.182
	35	29.283	10.714		35	21.028	6.121
	51	60.983	22.312		51	36.606	10.655
	60	38.538	14.100		60	32.902	9.577
Column 5 (Powdered limestone 2%)	2	31.588	100.000	Column 10 (Granulated limestone 5%)	2	639.150	100.000
	6	45.309	143.437		6	208.269	32.585
	12	17.402	55.091		12	104.137	16.293
	17	5.984	18.944		17	61.255	9.584
	25	13.996	44.308		25	66.737	10.442
	35	9.341	29.571		35	62.219	9.735
	51	17.497	55.391		51	108.772	17.018
	60	10.297	32.598		60	82.818	12.958

Table 5. Results of the pilot scale column experiment with the capping soil treatment (Zn)

	Time (month)	Conc. (㎍/L)	Leaching rate(%)		Time (month)	Conc. (㎍/L)	Leaching rate(%)
Column 1 (without amendment)	2	4924.568	100.000	Column 6 (Powdered limestone 5%)	2	27037.133	100.000
	6	2227.648	45.235		6	16740.649	61.917
	12	1225.114	24.878		12	12000.627	44.386
	17	2230.664	45.297		17	3392.674	12.548
	25	1748.474	35.505		25	1919.986	7.101
	35	739.061	15.008		35	1125.439	4.163
	51	864.047	17.546		51	655.314	2.424
	60	865.622	17.578		60	700.447	2.591
Column 2 (capping without amendment)	2	16530.598	100.000	Column 7 (Powdered apatite 2%)	2	24269.098	100.000
	6	7449.593	45.065		6	12877.920	53.063
	12	5311.833	32.133		12	3432.016	14.142
	17	2299.793	13.912		17	3164.606	13.040
	25	2881.446	17.431		25	3495.104	14.401
	35	1528.201	9.245		35	1906.529	7.856
	51	1651.343	9.990		51	1967.535	8.107
	60	-	-		60	2365.426	9.747
Column 3 (Powdered lime 2%)	2	23775.121	100.000	Column 8 (Powdered apatite 5%)	2	17299.934	100.000
	6	14087.749	59.254		6	10654.300	61.586
	12	9657.549	40.620		12	6043.152	34.932
	17	2407.108	10.124		17	1993.712	11.524
	25	2618.163	11.012		25	2277.477	13.165
	35	1607.127	6.760		35	1025.322	5.927
	51	1121.871	4.719		51	981.953	5.676
	60	965.021	4.059		60	1004.058	5.804
Column 4 (Powdered lime 5%)	2	8187.695	100.000	Column 9 (Granulated lime 5%)	2	12022.676	100.000
	6	5350.513	65.348		6	6692.665	55.667
	12	3850.249	47.025		12	3985.640	33.151
	17	2613.967	31.926		17	2681.145	22.301
	25	2612.018	31.902		25	2840.101	23.623
	35	856.396	10.460		35	1260.470	10.484
	51	150.435	1.837		51	415.400	3.455
	60	52.959	0.647		60	150.838	1.255
Column 5 (Powdered limestone 2%)	2	20099.385	100.000	Column 10 (Granulated limestone 5%)	2	33583.168	100.000
	6	13043.627	64.896		6	13305.638	39.620
	12	8034.487	39.974		12	8962.908	26.689
	17	2234.422	11.117		17	2290.804	6.821
	25	1912.961	9.518		25	3440.400	10.244
	35	883.873	4.398		35	1847.358	5.501
	51	825.415	4.107		51	1855.216	5.524
	60	685.425	3.410		60	2281.571	6.794

Table 6. Result of the pilot scale column experiment with the lime mixing treatment (As).

Column 1 (without mixing treatment)		Column 2 (Granulated lime 5%)		Column 3 (Granulated lime 10%)	
Time (month)	Conc. (㎍/L)	Time (month)	Conc. (㎍/L)	Time (month)	Conc.(㎍/L)
1	5.342	1	10.064	1	16.957
2	17.231	2	6.846	2	7.692
5	1.983	5	1.942	5	1.033
8	1.388	8	3.862	8	0.532
11	2.140	11	1.388	11	0.863
13	2.521	13	0.962	13	0.179
17	1.388	17	0.501	17	0.480
20	3.612	20	0.668	20	0.616
23	3.539	23	0.397	23	0.303
26	3.925	26	0.866	26	0.386
28	2.971	28	1.683	28	0.250
31	3.413	31	0.625	31	0.327
37	2.721	37	1.154	37	2.625
40	3.000	40	2.644	40	0.337
43	3.929	43	3.087	43	0.057
46	4.487	46	0.194	46	0.000
49	4.226	49	0.569	49	0.706
52	3.462	52	0.645	52	0.866
55	4.408	55	0.740	55	0.683
58	5.934	58	0.501	58	0.228
60	3.964	60	1.469	60	0.444

Table 7. Results of the pilot scale column experiment with the lime mixing treatment (Cd and Zn).

	Column 1 (without mixing treatment)		Column 2 (Granulated lime 5%)		Column 3 (Granulated lime 10%)	
	Time (month)	conc. (㎍/L)	Time (month)	conc. (㎍/L)	Time (month)	conc.(㎍/L)
Cd	1	217.385	1	1.213	1	0.64
	3	149.316	3	0.952	3	0.492
	5	145.650	5	0.952	5	0.448
	8	113.654	8	0.706	8	0.396
	10	107.962	10	0.834	10	0.395
	15	75.91	15	0.623	15	0.435
	20	70.256	20	0.776	20	0.529
	25	54.264	25	0.686	25	0.353
	35	47.158	35	0.808	35	0.449
	45	49.113	45	0.389	45	0.395
	55	44.750	55	0.401	55	0.296
	60	46.157	60	0.365	60	0.324
Zn	Column 1 (without mixing treatment)		Column 2 (Granulated lime 5%)		Column 3 (Granulated lime 10%)	
	Time (month)	conc. (㎍/L)	Time (month)	conc. (㎍/L)	Time (month)	conc.(㎍/L)
	1	17448.288	1	0.000	1	42.027
	3	12989.843	3	78.272	3	46.476
	5	12970.563	5	23.425	5	148.490
	8	9585.860	8	14.636	8	23.333
	10	9878.366	10	19.797	10	186.894
	15	7474.151	15	3.194	15	51.524
	20	6684.793	20	383.828	20	33.388
	25	5386.388	25	350.107	25	63.004
	35	3244.164	35	217.099	35	6.788
	45	3929.846	45	0.000	45	0.000
	55	3332.359	55	21.870	55	29.837
	60	3198.092	60	5.601	60	11.406