

Lime (CaO) and Limestone (CaCO₃) Treatment as the Stabilization Process for Contaminated Farmland Soil around Abandoned Mine, Korea

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폐광산 주변 중금속 오염 농경지 토양 복원을 위한 석회(CaO)와 석회암(CaCO₃)의 안정화 효율 규명

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국내 폐광산 주변 중금속 오염 농경지 토양 복원을 위해 석회(CaO)와 분쇄한 석회암(CaCO₃)을 안정화제로 이용한 토양 안정화 공법의 효율을 규명하는 배치 및 대형 칼럼실험을 실시하였다. 오염토양은 경북 군위군에 위치한 아연 폐광산 지역의 오염 농경지 토양을 이용하였으며, 안정화제의 함량은 오염토양 대비 0, 0.5, 2, 5%로 다양하게 적용함으로써, 안정화제에 의해 토양으로부터 용출되는 중금속 농도 변화를 시간에 따라 측정하여 안정화제의 중금속 저감 효율을 규명하였다. 배치실험 결과, 가루상의 석회나 석회암 0.5%를 토양과 혼합하여 안정화제로 사용한 경우, 오염토양으로부터 As, Cd, Pb, Zn의 중금속 용출 농도는 안정화제를 사용하지 않은 토양으로부터의 용출 농도를 기준으로 각각 70, 77, 94, 그리고 95% 감소하여 중금속 용출 저감 효과가 매우 높은 것으로 나타났다. 토양 개토법을 모사한 대형 칼럼실험 결과, 2% 입상 석회 첨가에 의해서 As, Cd, Zn의 토양 용출은 안정화제를 사용하지 않은 토양 용출 농도를 기준으로 각각 63, 97, 98% 감소하였다. 입상 석회암을 안정화제로 이용한 칼럼에서는 2% 석회암 첨가에 의해서 As의 용출 농도는 135.6 µg/L에서 30.2 µg/L 감소하여 약 46% 이상의 감소율을 나타내었으며, Cd와 Zn의 경우에는 97% 이상 감소하였다. 배치 및 칼럼실험 결과 석회암의 중금속 용출 저감 효율이 석회의 저감 효율과 매우 비슷한 것으로 나타나, 토양으로부터 중금속을 안정화 시키는데 입상 석회와 석회암 모두 효과가 매우 좋은 것으로 나타났다. 토양 산성화 방지를 위해 토양개량제로 주로 사용하였던 석회의 과도한 토양 내 첨가가 토양의 급격한 pH 증가를 일으켜 농작물 재배에 악 영향을 주게 되는 한계를 극복하기 위하여, 본 배치 및 대형 칼럼실험을 통하여 토양 내 첨가에 의한 pH 증가가 거의 없으며 비용 측면에서도 석회보다 훨씬 저렴하지만 중금속 용출 저감 효과가 비슷한 석회암이 중금속 오염 농경지 토양 복원을 위한 새로운 안정화제로 유용하게 사용될 수 있음을 입증하였다.

주요어 : 안정화, 고정화, 석회, 석회암, 중금속 오염

The mixing treatment process using lime (CaO) and limestone (CaCO₃) as the immobilization amendments was applied for heavy metal contaminated farmland soils around Goro abandoned Zn-mine, Korea in the batch and pilot scale continuous column experiments. For the batch experiments, with the addition of 0.5 wt.% commercialized lime or limestone, leaching concentrations of As, Cd, Pb, and Zn from the contaminated farmland soil decreased by 70, 77, 94, and 95%, respectively, compared to those without amendments. For the continuous pilot scale column experiments, the acrylic column (30 cm in length and 20 cm in diameter) was designed and granulated lime and limestone were used. From the results of column experiments, with only 2 wt.% of granulated lime, As, Cd, and Zn leaching concentrations decreased by 63%, 97%, and 98%, respectively. With 2 wt.% of granulated limestone, As leaching concentration reduced from 135.6 to 30.2 µg/L within 5 months and maintained mostly below 10 µg/L, representing that more than 46% diminution of leaching concentration compared to that without the amendment mixing. For Cd and Zn, their leaching concentrations with only

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2 wt.% of limestone mixing decreased by 97%, respectively compared to that without amendment mixing, suggesting that the capability of limestone to immobilize heavy metals in the farmland soil was outstanding and similar to that of lime. From the column experiments, it was investigated that if the efficiency of limestone to immobilize heavy metals from the soil was similar to that of lime, the limestone could be more available to immobilize heavy metals from the soil than lime because of low pH increase and thus less harmful side effect.

Key words : stabilization, immobilization, lime, limestone, heavy metal contamination

1. Introduction

High concentration of heavy metals such as cadmium (Cd), lead (Pb), zinc (Zn), mercury (Hg), nickel (Ni) and arsenic (As) leached from soils may cause long term risks to ecosystem and humans (EPA, 1992; Raskin and Ensley, 2000; Harvey *et al.*, 2002). Although heavy metals were released in varying quantities into soils from parent rocks, increasing environmental contamination has been mainly caused by human activities such as mining, smelting, agricultural practices and waste disposal (Alloway, 1995; Christensen 1999; Sasowsky *et al.*, 2000). Most of abandoned mines in Korea have been contaminated with arsenic and other heavy metals from tailings and waste ore rock fragments (KARICO, 2004; MOE, 2005; Cha *et al.*, 2003). Continuous leaching of these metals to the sub-surface by contaminated groundwater and surface water, and the down stream movement and deposition of mine tailings on the farmland soils generated their accumulation in farmland products at contaminated sites.

One of main processes to control heavy metal contaminated farmland soils was to decrease the extraction or leaching rate of heavy metals by using of soil immobilizing amendments, called "stabilization method" (Wiles, 1987; Corner, 1994). Many stabilization technologies have been applied as a last approach to the management of hazardous waste (Cullinane *et al.*, 1986; Jones, 1990; Silva *et al.*, 2007; Shi and Fernandez-Jimenez, 2006). Among them, in-situ chemical immobilization process is based on the use of amendments to accelerate immobilization processes such as sorption, precipitation and complexation reactions, that take place naturally in soils to reduce mobility and bio-availability of heavy metals (Leist *et al.*, 2003; Halim *et al.*, 2005; Wang *et al.*, 2001; Chlopecka and Adriano, 1996). While physico-chemical extraction techniques such as soil washing 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 sites (EPA, 2000). In heavy metal contaminated soils around abandoned mines, the immobilization process is mostly based on additions of cement, glass fiber, coal fly ash, and gypsum (Matlock *et al.*, 2002; Ahn *et al.*, 2002; Yukselen and Alpaslan, 2001; Li *et al.*, 2001). One of the cheapest and the most effective material for stabilization was lime (CaO) and lime-based stabilization could be an effective remediation alternative for the immobilization of arsenic or other heavy metals in contaminated soils (Clifford *et al.*, 1986; Bell, 1996; Schifano *et al.*, 2006; Lee *et al.*, 2006). However, the pH increase according to the addition of lime to soil has been serious limitation to apply the lime as a stabilization amendment to the real field.

This research focused on the soil stabilization process by using not only lime but also limestone (CaCO₃) to decrease the leaching of arsenic and other heavy metals from contaminated farmland soils around an abandoned mine, Korea. Batch experiments were performed to investigate the efficiency of lime and limestone as immobilizing amendments to reduce the heavy metal leaching from the contaminated soil. Pilot scale column as a physical model for the genuine contaminated soil environment was designed and heavy metal leaching rates by artificial rainfall were measured in diverse treatment conditions. The research for the efficiency of limestone to immobilize heavy metals from soil in the stabilization process is very limited. The main objective of this research is to investigate the efficiency of "mixing soil treatment" using limestone as well as lime to immobilize heavy metal from the contaminated soil by lab scale experiments.

2. Experimental Method

2.1. Properties of contaminated soil, lime, and limestone for the experiments

Heavy metal contaminated soils were sampled at the farmland (a rice paddy field) beside of the main stream connected to Goro abandoned Zn-mine, which is located at Gunwi county, Korea. Goro abandoned 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 (Lee *et al.*, 2004). Most of mine tailings were washed away during the flood seasons and contaminated farmland and the stream connected with the mine. Eighty kilograms of surface soils were collected at the farmland, which was 500 m down away from the tailing storage site of the Goro mine. Soil samples were dried in oven at 30°C for 2-4 day and sieved at 2 mm in diameter. Physical and chemical properties of soil samples such as pH, TOC (total organic carbon content), and grain size, which directly affect leaching properties of heavy metals from soils, were measured. TOC was measured using a CHN (carbon, hydrogen, nitrogen) analyzer (Thermo Finnigan Flash EA 1112), and pH of contaminated soil was measured by electrode (Istek, 815PDC) via a distilled water extraction method (soil:distilled water = 1:5). Grain size distribution of soils was also measured through the dry-sieving and pipetting method. For the reliability of experimental data, the measurement of pH, TOC, and grain size analysis were repeated for three soil samples, and their arithmetic mean were determined as the final values of the soil. If any of them was over 5% of their arithmetic mean, the results were ignored and the experiment was duplicated. From the grain size analysis, mass ratio of sand, silt, and clay for the soil was 35 wt.%, 60 wt.%, and 5 wt.%, respectively, suggesting that the textural domain of contaminated soil was "silt loam" (USDA, 2007). Five

mass (each of 50 g) were randomly collected from the soil sample and analyzed using an ICP-OES (Perkin Elmer, Optima 3300XL) to determine heavy metal concentrations, following the Korean Standard Procedure for Soil Analysis enacted in 1995 (MOE, 2003). The arithmetic mean of each heavy metal concentration for five soil samples was accepted as the representative concentration. Heavy metal concentrations, pH, and TOC of the soil are shown in Table 1.

For the experiments, ACS grade lime and limestone ("A type" lime and limestone purchased from Shinyo Pure Chemicals Co. Ltd., Japan; CaO and CaCO₃ purity > 98%) and lime and limestone commercially produced from a fertilizer plant ("B type" lime and limestone purchased from Hanil Co. Ltd., Korea) were used as immobilization amendments. For the batch experiments A and B type of lime and limestone were used and for the pilot scale column experiments, only B type of lime and limestone were used as amendments because of their economic considerations. The principal component analysis of B type lime and limestone was performed by X-ray fluorescence spectrometer (Shimadzu, XRF-1700) and the result is shown in Table 2. Because amount of the amendment affects the immobilization efficiency of heavy metals in soil, various amounts of amendments were used in the experiments (0, 0.5, 2, and 5 wt.% of soil mass). Powdered lime and limestone were used in batch experiments and granulated lime and limestone (4~6 mm in diameter) were used in column experiments.

2.2. Batch experiments

Dried contaminated soil, sieved with No. 10 mesh (2 mm in diameter) was mixed with powdered lime (A or B type of lime) at various ratio (0, 0.5, 1, 2, and 5 wt.% of soil). Total 20 grams of soil, including lime was immersed with 500 ml of distilled water (titrated at pH 6) in a 500 ml Teflon capped flask. Flask was shaken at 20°C and 100

Table 1. Properties of the farmland soil for the experiment

	Heavy metal concentration (mg/kg)				pH	TOC (wt.%)
	As	Cd	Pb	Zn		
Contaminated farmland soil	198.15	8.36	790.90	486.87	5.3	0.13
KSPWL	6.00	1.50	100.00	300.00	-	-

*KSPWL: Korea Soil Pollution Warning Limit

Table 2. Results of XRF principal component analysis for B type lime and limestone

	Chemical composition by XRF-analysis (units: wt.%)								total
	CaO	MgO	SiO ₂	Fe ₂ O ₃	SO ₃	Al ₂ O ₃	As ₂ O ₃	Na ₂ O	
Lime	94.9	0.0	4.0	0.5	0.1	0.4	0.0	0.0	99.9
Calcium carbonate	96.6	0.0	0.7	0.0	2.1	0.2	0.0	0.6	100.2

rpm in the thermohydrostat. While the flask was shaken, 10 ml of equalized solution was sampled every 12 hr, 24 hr, 72 hr, and 120 hr. It was centrifuged, and filtered by filter paper (5B) for heavy metal analysis on ICP/OES to determine leaching concentration of As, Cd, Pb, and Zn from soil in the batch experiments. For each batch experiment, the leaching concentration for each specific heavy metal from the contaminated farmland soil was measured on the conditions of diverse amounts of amendments. By using A and B type limestone as amendments, the batch experiments were repeated to investigate the efficiency of limestone on the immobility of heavy metals from the soil and their results were compared with those of lime. For the reliability of experimental data, the arithmetic mean of three batch experiments was accepted as the representative results. If any of them was over 20% of their arithmetic mean, the results were ignored and the experiment was duplicated.

2.3. Column experiments

Pilot scale continuous column experiments as physical model for genuine contaminated soil environment with an artificial rainfall condition were performed to investigate the decrease of heavy metal leaching by using "the mixing treatment" with immobilization amendments. An acrylic column (19 cm in diameter and 30 cm in height), which of the upper and lower parts consist of

dense lattice screen plates and the drain system for injection and extraction of artificial rainfall, was used for the column experiments. The average amount of rainfall per month around Goro mine was 91.2 mm per unit area, which was determined as artificial rainfall for the column experiments. However, only one-third of rainfall was considered to flow down into soil medium, which was sprayed on the top of the column every 12 hr. According to the amount of rainfall sprayed into the column, 12 hr in the column experiment represented to one month duration in the real field condition.

Contaminated farmland soil sample was dried at 30°C and sieved with No. 10 mesh (2 mm in diameter). As the amendments, granulated B type of lime and limestone (4~6 mm in diameter) were used for the "mixing treatment" experiment. Each column was packed with coarse size (0.4-0.6 mm in diameter) Ottawa sand at the bottom of column (2 cm in thickness). Two or 5 wt.% of granulated lime or limestone was well mixed with the farmland soil and packed on the top of the Ottawa sand (in 10 cm thickness). Coarse size Ottawa sand covered on the top of soil layer at 2 cm thickness. At every 12 hr, 817.15 ml of artificial rain (33% of average monthly rain fall) was uniformly sprayed on the top of the column at the constant rate of 200 ml/min for thirty days, representing 5 year of soil leaching in the real farmland field. Discharged water was sampled from the bottom of the column

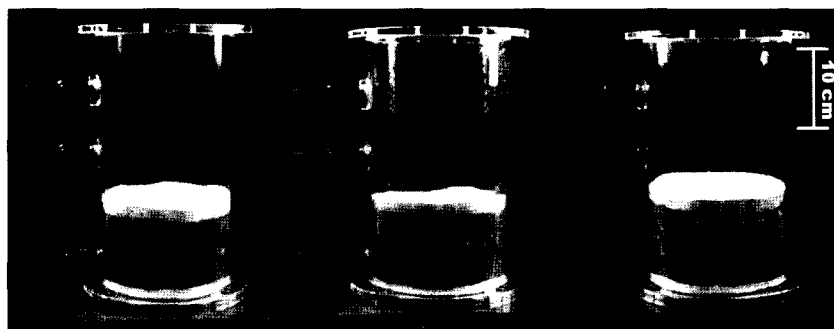


Fig. 1. Pilot scale continuous column experiment with lime mixing (from the left, 0, 2, and 5 wt.% lime mixing column).

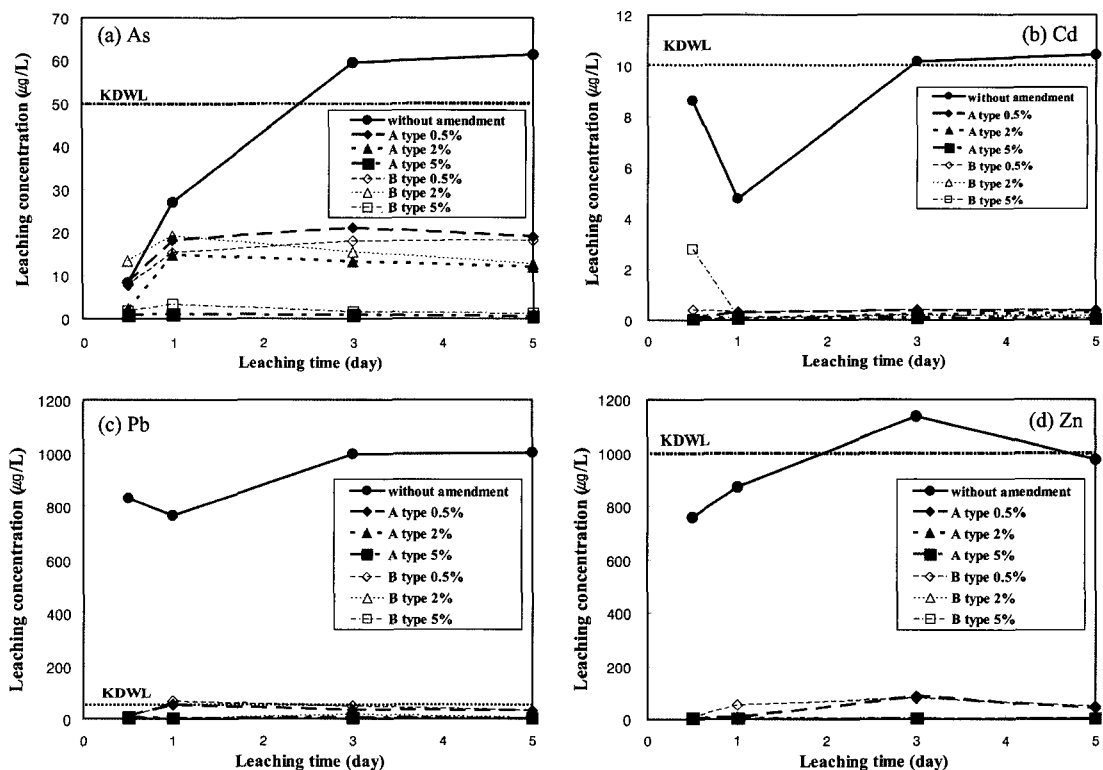


Fig. 2. Results of the batch experiments with lime mixing ((a) As, (b) Cd, (c) Pb, and (d) Zn).

at different time interval. The pH of discharged water was measured and its heavy metal leaching concentrations were analyzed on ICP/OES. From the column experiments, the accumulative mass of each heavy metal leached from the soil for 5 year was calculated to investigate the efficiency of lime and limestone on the immobilization of heavy metals. Fig. 1 shows the column experiment for the "mixing treatment".

3. Results and Discussions

3.1. Batch experiments

The leaching concentrations of heavy metals in the batch experiments using powdered lime and limestone are shown in Fig. 2. Leaching concentrations for all heavy metals without amendment (0 wt.% of lime or limestone) increased with the increase of leaching time and they maintained to higher than Korean Drinking Water Limits (KDWL) for 5 day leaching. For As, the leaching concentration without the amendment from the contaminated farmland soil increased from 8.28

µg/L to 61.36 µg/L, which maintained at higher than KDWL (50 µg/L). However, by the mixing of 0.5 wt.% lime, As leaching concentration decreased to one-third of its concentration without lime addition, and to one-fiftieth with 5% lime addition (Fig. 2(a)). As leaching concentration from the soil maintained much lower than KDWL with only 0.5% of A or B type lime. For other heavy metals such as Cd, Pb, and Zn, the effect of lime addition on their leaching concentration decreases was much more patent. With only 0.5 wt.% of lime addition, Cd leaching concentration decreased and maintained lower than 0.04 µg/L, which fell under only 4% of the leaching concentration in the case of without lime addition (Fig. 2(b)). Zn and Pb leaching concentrations by the addition of 0.5 wt.% A or B type lime decreased by 95%, which was very similar to the result of Cd concentration (Fig. 2(c) and (d)). From the results of the batch experiments, leaching concentrations of all heavy metals could be decreased much lower than KDWL by only the addition of 0.5% lime. There existed no big difference in the leaching concentration de-

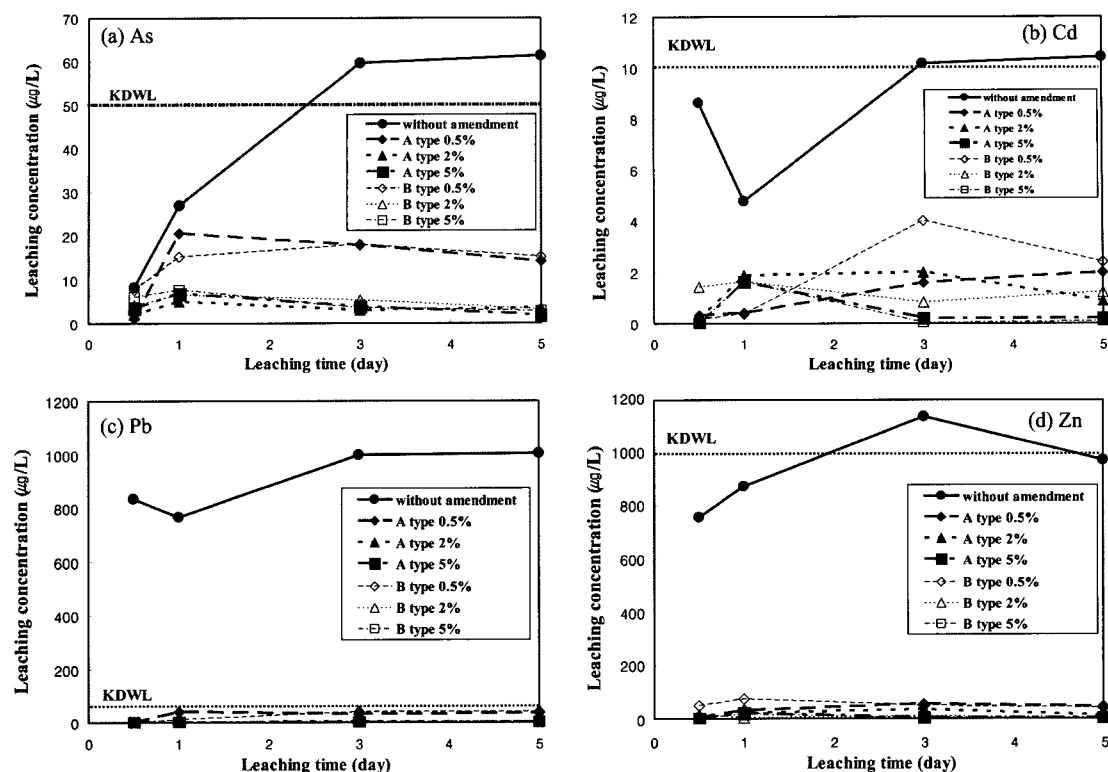


Fig. 3. Results of the batch experiments with limestone mixing ((a) As, (b) Cd, (c) Pb, and (d) Zn).

crease between A type and B type lime, suggesting that B type lime, which is much cheaper than A type lime, could be used in the real contaminated sites.

The results of leaching concentrations using A and B type limestone are shown in Fig. 3. While the amount of limestone increased, leaching concentrations of heavy metals mostly decreased, which were similar to those of lime addition. As leaching concentration reduced to one-fourth of the concentration with only 0.5 wt.% of limestone addition, and to one-twentieth with 5% limestone addition, suggesting that limestone is more effective on As immobilization from the soil in the case of small amount addition, compared with lime (Fig. 3(a)). Cd leaching concentration decreased by 80% with 0.5 wt.% of A type limestone and 77% with 0.5 wt.% of B type limestone, suggesting that the limestone is less effective to immobilize Cd from the soil than the lime (Fig. 3(b)). For Pb, and Zn leaching concentrations, they reduced by 95% with only 0.5 wt.% of limestone, of which results were very similar to those of lime addition (Fig. 3(c)

and (d)).

Instead of its amazing efficiency on the reduction of heavy metal leaching from the soil, the worst defect of the lime to soil was the unexpected pH increase of leaching solution and soil. It was reported that the transition of soil pH to above 12 adversely affects on the plant growth and on the contrary of our results, may increase the leaching rate of specific heavy metals such as As and Pb from the soils (Brady and Weil, 2001). Table 3 shows the pH change of the leaching solution by the addition of lime or limestone in the batch experiment. The initial pH of contaminated farmland soil was 5.3 falling on the weak acid condition. However, by the addition of 2 wt.% lime, the pH of the leaching solution in the batch experiments increased to 11.0. Even the pH of solution decreased somewhat by the buffering effect of the soil as time went by, it maintained above 10.0. Even 5 wt.% limestone was added as an amendment in the batch experiments, the pH of leaching solution slightly increased and maintained lower than 9 (mostly around 8), but its efficiency to immobilize

Table 3. pH of leaching solution at batch experiments

Soil type	pH of leaching solution		
	0.5 day leaching	1 day leaching	3 day leaching
Without amendment	6.1	7.7	7.0
A type 2% lime addition	11.2	11.3	11.0
A type 5% lime addition	11.2	12.0	11.5
B type 2% lime addition	10.9	10.5	10.1
B type 5% lime addition	11.2	11.6	11.8
A type 2% limestone addition	8.3	8.6	7.6
A type 5% limestone addition	8.4	8.4	7.9
B type 2% limestone addition	8.2	8.3	8.1
B type 5% limestone addition	8.2	9.0	8.0

heavy metals from the soil was similar to that of lime, suggesting that limestone could be more available to immobilize heavy metals from the soil than lime because of less harmful side effect and economic consideration.

3.2. Column experiments

The results of leaching concentration with the lime amendment in the column experiments are shown in Fig. 4. The initial As concentration of leached water from the bottom of the column without the amendment was 172.3 $\mu\text{g/L}$ and decrease to 19.8 $\mu\text{g/L}$ within 5 month of artificial rain fall. It maintained at the range of 13.9-59.3 $\mu\text{g/L}$ (the arithmetic mean: 42.4 $\mu\text{g/L}$) for 5 year leaching (Fig. 4(a)). With 2 wt.% of lime mixing treatment, As leaching concentration decreased from 100.6 $\mu\text{g/L}$ to 19.4 $\mu\text{g/L}$, and maintained below 10 $\mu\text{g/L}$ (the arithmetic mean: 15.5 $\mu\text{g/L}$), showing that As leaching concentration decreased by 63% with 2 wt.% of lime mixing, and by 70% with 5 wt.% of lime. The initial Cd concentration of leaching solution without the amendment was 217.4 $\mu\text{g/L}$ and maintained above 45 $\mu\text{g/L}$, which is 4.5 times of KDWL (10 $\mu\text{g/L}$). However, with only 2 wt.% of lime, Cd leaching concentration reduced below 2 $\mu\text{g/L}$ (arithmetic mean: 2.9 $\mu\text{g/L}$), decreasing by 97% compared with that without the lime addition (Fig. 4(b)). The average leaching concentration of Zn from the column without the lime addition for 5 year was 801.0 $\mu\text{g/L}$, but it dramatically decreased to 14.0 $\mu\text{g/L}$ with 2 wt.% of lime mixing and to 6.3 $\mu\text{g/L}$ with 5 wt.% of lime (Fig. 4(c)). Table 4 shows the total mass of each heavy metal leached out from the soil column for 5 year. The mass of As, Cd, and Zn leached from the soil column

without the amendment for 5 year was 1.84, 2.70, and 23.21 mg, respectively. However, by the addition of 2 wt.% granulated lime (B type), leached mass of As, Cd, and Zn were reduced to 0.57, 0.10, and 0.45 mg, suggesting that only 2 wt.% of lime dramatically immobilize heavy metal from the soil.

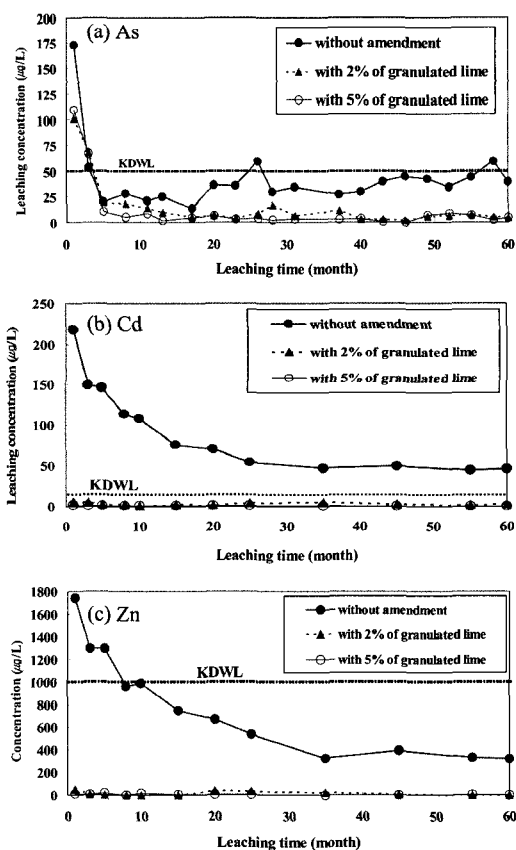


Fig. 4. Results of the column experiments with lime mixing ((a) As, (b) Cd, and (c) Zn).

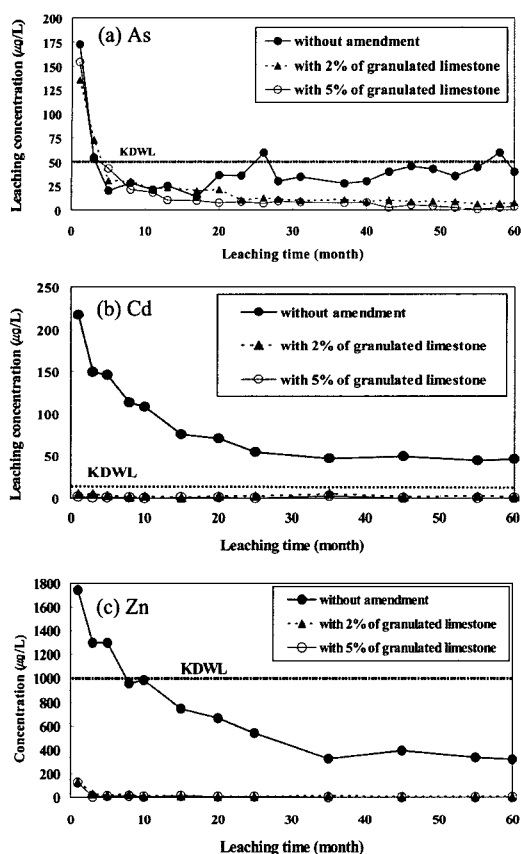


Fig. 5. Results of the column experiments with limestone mixing ((a) As, (b) Cd, and (c) Zn).

The results of the column experiments by using granulated limestone as an amendment are shown in Fig. 5. With 2 wt.% of granulated B type limestone, As leaching concentration reduced from 135.6 to 30.2 µg/L within 5 month and maintained mostly below 10 µg/L, representing that more than 46% diminution of leaching concentration compared to that without the amendment mixing (Fig. 5(a)). With 5 wt.% of limestone mixing, As leaching concentrations maintained to less than 5 µg/L

(its average for 5 year leaching decreased by 55%). From the results of the column experiments, As immobilization capability of limestone was little lower than that of lime, but much enough to maintain its leaching concentration to lower KDWL (50 µg/L). For Cd, their leaching concentrations with 2 or 5 wt.% of limestone mixing decreased by 97 and 99%, respectively compared to that without amendment mixing, suggesting that the capability of limestone to immobilize Cd in the farmland soil was outstanding and similar to that of lime (Fig. 5(b)). With 2 wt.% of granulated limestone mixing, Zn leaching concentration decreased to less than 10 µg/L leaching in the column, and the average Zn leaching concentration for 5 year decreased by 97% (arithmetic mean: 21.4 µg/L) compared to that without the amendment mixing (Fig. 5(c)). With only 2 wt.% of granulated limestone mixing, the total mass of As, Cd, and Zn leached from the contaminated farmland soil decreased by 53%, 97%, and 98% for 5 year, compared to those without the amendment (Table 4). From the results of column experiments, the capability of limestone to immobilize As, Cd and Zn from the farmland soil was little less than that of lime, suggesting that the "limestone mixing treatment" process has great possibility to immobilize heavy metals from the soil.

Fig. 6 shows the pH change of leaching solution according to the addition of lime and limestone in the column experiments. When 2 wt.% of granulated lime was mixed with the soil, the pH of leaching solution increased from 6.2 to 12.3 at the early stage, and then maintained about 11.5 for 5 year leaching. However, while 5% of granulated limestone was used, the pH of leaching solution was mostly lower than 7.0 for the column experiments. If the efficiency of limestone to immobilize heavy metals from the soil was similar to that of lime, the limestone could be more available to

Table 4. Estimated total mass of heavy metals leached from the soil in the column for 5 year

Soil type	Total mass (mg) leached from the soil for 5 year		
	As	Cd	Zn
Contaminated farmland soil without amendment	1.84	2.70	23.21
2% granulated lime mixing	0.57	0.10	0.45
5% granulated lime mixing	0.40	0.02	0.16
2% granulated limestone mixing	0.87	0.09	0.44
5% granulated limestone mixing	0.62	0.03	0.28

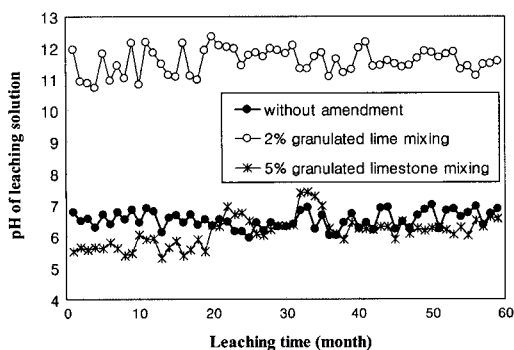


Fig. 6. pH change of leaching solution from the soil column for 5 year.

immobilize heavy metals from the soil than lime because of low pH increase and thus less harmful side effect. From the results of the batch and column experiments, it was investigated that the mixing treatment process with limestone as well as lime has a great possibility to immobilize heavy metals from the farmland soils around the abandoned mine.

4. Conclusion

From the results of the batch experiments, by using 0.5 wt.% lime, As leaching concentration from the farmland soil decreased to one-third of its concentration without the amendment mixing and decreased to one-fiftieth by using 5% lime. For Cd, Pb, and Zn, the capability of lime to immobilize them was much more patent than in As and their leaching concentrations decreased by more than 95% with only 0.5 wt.% lime mixing. The capability of limestone to immobilize heavy metals was similar to that of lime, suggesting that both of lime and limestone are very useful to lower the leaching concentration of heavy metals from the contaminated soils.

From the results of the continuous pilot scale column experiments, with only 2% of granulated lime, As, Cd, and Zn leaching concentrations decreased by 63%, 97%, and 98%, respectively, compared to that without the amendment mixing and they maintained much below KDWL for 5 year leaching. Even the pH of leaching water increased according to the lime addition, most of As were remained in soil during the "mixing treatment", suggesting that some of As were dissolved at high

pH condition at first but they were immediately re-precipitated as forms such as calcium carbonate and/or clay-organic complexes.

By using granulated limestone, the decrease of heavy metal leaching from the soil was very similar to that with lime in the column. From the batch and the continuous column experiments, it was investigated that the "mixing treatment" using lime and limestone will become one of major processes to immobilize heavy metals from the contaminated soils around abandoned mines. Because of low pH change, less adverse effects, and economical consideration, limestone could be more available to immobilize heavy metals from the farmland soil than lime in the real contaminated site.

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