Research Article

Immobilization of Cd, Zn, and Pb from Soil Treated by Limestone with Variation of pH Using a Column Test

Sung-Wook Yun¹ and Chan Yu^{1,2}

¹Institute of Agriculture & Life Science, Gyeongsang National University, 900 Gazwa, Jinju, Gyeongnam 660-701, Republic of Korea

²Department of Agricultural Engineering, Gyeongsang National University, 900 Gazwa, Jinju, Gyeongnam 660-701, Republic of Korea

Correspondence should be addressed to Chan Yu; chanyu@gnu.ac.kr

Received 14 January 2015; Revised 11 March 2015; Accepted 11 March 2015

Academic Editor: Chengshuai Liu

Copyright © 2015 S.-W. Yun and C. Yu. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Decades of mining in South Korea have resulted in the contamination of large amounts of soil by metals. The most feasible approach to site restoration requires the use of a stabilization agent to reduce metal mobility. This study examined the leaching characteristics of limestone used as a stabilization agent when subjected to solutions of differing pH. In a laboratory-scale column test, solutions with pH values of 3.5, 4.6, and 5.6, representing acidic to nonacidic rainfall, were applied to soil mixed with limestone. Test results indicate that metal components can be released with the addition of acidic solutions, even if the soil is highly alkaline. Cd and Zn, in particular, exhibited abrupt or continuous leaching when exposed to acid solutions, indicating the potential for contamination of water systems as metal-laden soils are exposed to the slightly acidic rainfall typical of South Korea. Treatment using stabilization agents such as limestone may reduce leaching of metals from the contaminated soil. Stabilizing metal-contaminated farmland is an economical and feasible way to reduce pollutants around abandoned metal mines.

1. Introduction

Contamination by mining activities is one of the most serious causes of soil quality degradation [1]. About 1,104 metal mines have been documented in South Korea, and 1,069 of those (97%) were abandoned after closure [2]. The tailings and wastes from these abandoned metal mines (AMMs) have significantly polluted nearby farmlands [3], and the resulting metal accumulation in crops poses a serious environmental threat to human health [4, 5], since neither are metals removed from the soil nor do their contents decrease [6]. The general approach for the remediation of metal-contaminated areas, therefore, is to excavate the contaminated soil and reclaim the land with clean soil. This method, however, not only is costly but also can lead to secondary contamination. It is also known to be destructive to the ecosystem [7–9].

Stabilization, an *in situ* technique, uses a stabilization agent to reduce the mobility and bioavailability of metals and is considered to be both economical and efficient [3, 8]. Many studies have examined different stabilization agents and their mechanisms for reducing the mobility and bioavailability of metals in soil. According to Kumpiene et al. [10] and Ruttens

et al. [6], it could be accomplished by increasing the pH of the soil, and alkaline materials are the most widely used to stabilize metal-contaminated soil. However, the durability of this method has not been proven, and treated areas require regular monitoring [11]. Still, until a more economical and effective remediation technique is developed, stabilization remains the most feasible alternative for the remediation of metal-polluted soils.

In South Korea, national environmental regulations stipulate the total content of metal in the soil, and therefore, it is not easy to set a remediation goal or to evaluate the results of stabilization. However, if polluted areas are left as they are, contamination may spread to the surrounding environment via rainfall or wind. Normal rain is slightly acidic with a pH = 5.6 and could accelerate the mobility of metals, whose solubility increases under weakly acidic conditions. Additionally, incidences of acid rain are expected to increase in severity as smog-laden air masses from China move into South Korea.

Further, in South Korea, the great majority of soils near AMMs are contaminated with Zn, Cd, and Pb [12]. In most cases, these components are distributed in contaminated

TABLE 1: pH and XRF analysis results of the soil amendment used in this study.

Amendment	pH	XRF ¹ analysis (%)						
		SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	MnO	P ₂ O ₅
Limestone	9.60	12.7	2.89	3.24	62.7	14.9	0.52	0.06

¹X-ray fluorescence spectrometer.

soil in the form of various composites; the cases of single-component contamination are extremely rare. Therefore, the applicability of a stabilization method should be examined with respect to Cd, Zn, and Pb, without limiting to a specific single component.

This study investigates the long-term performance of stabilization with variation of pH. Limestone was applied as a stabilization agent in a laboratory-scale column test, and the leaching characteristic of the metal components, that is, Cd, Zn, and Pb, in the soil sample was observed and compared to the results of the control soil sample.

2. Materials and Methods

2.1. Soil Sampling. A representative soil sample was collected from farmland near Seosung Mine, located in Jigok, Seosan City, Chungnam Province, South Korea. Interviews with residents around the abandoned mine site indicated that tailings from the mine had been used periodically to replace the topsoil of farmlands. The farmlands have been left fallow because of metal contamination from mining activity. The soil was sampled using a shovel according to the Standard Method for Soil Analysis [13]. The sampled soil was transported to the laboratory, spread on a pan at a uniform thickness, and air-dried for a week. The specimen was sieved with a 2 mm sieve for physicochemical and metal analyses and with a 9.54 mm sieve for the column test.

2.2. Stabilization Agent. In this study, limestone (<2 mm) was used as the stabilization agent. In South Korea, limestone has been used as a stabilization agent for a long time because it is abundant and inexpensive. Calcareous materials increase soil pH and thus induce an increase in the soil's negative charge, which in turn induces the cationic metals to be adsorbed and precipitated onto the soil surface [14]. The technical manual of Korea Mine Reclamation Corp. states that both agents should be crushed to a particle size of less than and equal to 2 mm [15]. Table 1 shows the results of the pH and XRF analyses for the limestone used.

2.3. Procedure of Laboratory-Scale Column Test. Acrylic columns manufactured for the experiments had a thickness, inner diameter, and height of 0.5, 10, and 80 cm, respectively, as shown in Figure 1. Two gate valves were installed at the top and bottom of each column to control irrigation and drainage. A 5 cm thick sand filtration layer was placed beneath the contaminated soil layer. Standard sand of Korean standard (KS L IOS 679), which had been sterilized for 30 min in an autoclave (KT4422, Kasteck, Korea) at 121°C, was used as the filter layer. Limestone was mixed with the

TABLE 2: Physical properties of the untreated and treated soils in the soil columns.

Amendment	Void ratio	Dry unit weight (g/cm ³)	Pore volume (mL)
Untreated control	0.76	1.49	2,026
Limestone treated	0.73	1.51	1,988

contaminated soil using a 5% mixing ratio (w/w, based on dried weight), which is a general design value of the Mireco [15] manual. The control column was filled with contaminated soil only (see also Figure 1). Five contaminated or treated soil layers were compacted by 15 blows from a 20 cm height using a 2.38 kg rammer to increase *in situ* density. Table 2 shows the physical characteristics of the soil samples treated in the column.

Acidic solution was applied to the top of columns and maintained at a constant depth of 6 cm during the test period. Leachate collected from the bottom of columns at 1 pore volume (PV) intervals. 1 PV corresponds to approximately 255 mm of rainfall; as the annual precipitation in South Korea is approximately 1,800 mm, 30 PV corresponds to the precipitation of approximately 4 and a quarter years. The solution for the test was made by mixing H₂SO₄ and HNO₃ (3:1 mole ratio) and diluting with distilled water to adjust the pH. The pH levels of the solutions were chosen to mimic the pH values of normal rainfall (5.6) and the average and minimum pH values in South Korea during 2006 (4.8 and 3.6, resp.) based on data from the Korea Ministry of Environment [16]. The different solutions were consecutively introduced into the soil column at 10 PV intervals. The entire leachate volume (30 PV) was collected from the columns. Before leaching, the control and treated soils in the columns were adjusted to 70% of field capacity moisture content and incubated for 2 days at room temperature. Columns were allowed to drain for 24 hr before next acidic solution was applied.

2.4. Quality Analysis of Soil and Leachate. The physicochemical soil characteristics were analyzed according to NIST [17]. The pH (soil < 2 mm) was measured using a pH and EC meter (Orion 550A, Thermo) at a 1:5 soil/distilled water ratio. The available phosphate (soil < 2 mm) was measured via the Lancaster method using a spectrophotometer (UV-1650 PC, Shimadzu, Japan). The exchangeable cations (soil < 2 mm) were extracted using 1 M NH₄OAc (pH 7) and were measured using an inductively coupled plasma spectrometer (ICP/OES, Optima 5300DV, Perkin Elmer). The soil texture was measured by the hydrometer and sieve method.

The metal contents of the soil (<0.15 mm) were measured via *aqua regia* digestion (3:1, v/v, HCl+HNO₃) using an

FIGURE 1: Diagram of the laboratory-scale column test for rainfall acidity simulation.

ICP/OES (Optima 5300DV, Perkin Elmer, USA), according to the Standard Method for Soil Analysis [13].

To investigate the fraction of metals in the soil (<0.15 mm), sequential extraction was performed using a modified BCR procedure. Four operationally defined fractions are acid soluble fraction (F1, soluble and exchangeable fraction and bound to carbonates, 0.11 M CH_3COOH , for 16 h), reducible fraction (F2, bound to Fe/Mn oxides, 0.5 M $\text{NH}_2\text{OH}\cdot\text{HCl}$, pH 2, for 16 h), oxidizable fraction (F3, bound to organic matter and sulfides, 30% H_2O_2 acidified with HNO_3 to pH 2 at 85°C for 2 h and then followed by the extraction with 1 M $\text{CH}_3\text{COONH}_4$, pH 2-3, for 16 h), and residual fraction (*aqua regia* digestion). At the end of each sequential extraction step, before injecting the extraction solution of the next step, the sample was washed with distilled water to prevent residual components causing error. In addition, the sample was passed through a centrifugal separator to prevent any loss of the sample when effluent was collected. The metal components of all collected extracts were measured by ICP-OES (Optima 5300DV, Perkin Elmer, USA).

The leachate quality collected was analyzed using the pretreatment and analysis procedure according to the Standard Method of Water Analysis [18]. The pH and EC values were measured using a pH and EC meter (Orion 550A, Thermo, Japan), and the Cd, Pb, and Zn contents were measured using an ICP/MS (ELAN DRC II, Perkin Elmer, USA).

2.5. Data Analysis. The Pearson correlation of the physicochemical soil characteristics, metal content statistics, pH values of the leachates, EC, and Cd, Pb, and Zn contents were analyzed using SPSS 12.0; Sigmaplot 10.0 was used to plot the graphs.

3. Results

3.1. Soil Characteristics. Table 3 shows the physicochemical characteristics and total metal contents of the soil used. The soil pH was 7.3, which is significantly higher than the reported value of 5.6 for farmlands in South Korea [19]. This may be due to the large quantity of crystalline limestone intercalated in the schist bedrock of the study area [20]. The contents of exchangeable calcium, magnesium, and potassium were 4.09, 0.84, and $0.37 \text{ cmol}^+/\text{kg}$, respectively. Lee et al. [21] reported that the pH value of the soils surrounding the AMM sites in South Korea ranged between 5.2 and 7.0 (average pH 5.8), and the contents of exchangeable calcium, magnesium, and potassium ranged between 1.4 and 18.3, 0.3 and 9.4, and 0.02 and $1.3 \text{ cmol}^+/\text{kg}$, respectively. The Cd, Pb, and Zn contents of the soil were 90.8 mg/kg, 8,058 mg/kg, and 5,196 mg/kg, respectively, which significantly exceed the national limit of soil quality [22].

The results of sequential extraction analysis on heavy metals for soil sample are shown in Table 4. The acid

TABLE 3: Physicochemical properties and total heavy metal content of the soil used in this study.

Parameter	Value ⁴
pH	7.3 ± 0.3
Av. P ₂ O ₅ (mg/kg) ¹	546 ± 35.8
Exch. cation (cmol/kg) ²	
Ca ²⁺	4.09 ± 0.78
Mg ²⁺	0.84 ± 0.15
K ⁺	0.37 ± 0.05
Soil texture (%)	
Sand	40
Silt	58
Clay	2
Metals (mg/kg) ³	
Cd	90.8 ± 4.52
Pb	8,058 ± 105
Zn	5,196 ± 112

¹ Available phosphate.² Exchangeable cation.³ The total heavy metal content was digested via *aqua regia* according to the standard method of soil pollution. The soil quality standards of Cd, Pb, and Zn in South Korea are 4, 200, and 300 mg/kg, respectively.⁴ The figures are the averages and standard deviations of three replicates.

TABLE 4: Results of sequential extraction of Cd, Pb, and Zn in soil sampled.

Fraction	Heavy metal (mg/kg)		
	Cd	Pb	Zn
F1 ^a	22.5 (27.2%) ^c	1,395 (18.6%) ^c	1,095 (22.8%) ^c
F2 ^b	6.56 (7.95%) ^c	548 (7.30%) ^c	292 (6.06%) ^c
F3 ^c	15.4 (18.6%) ^c	4,074 (54.2%) ^c	1,710 (35.6%) ^c
F4 ^d	38.1 (46.2%) ^c	1,495 (19.9%) ^c	1,713 (35.6%) ^c

^a Acid soluble fraction (soluble and exchangeable fraction and bound to carbonates).^b Reducible fraction (bound to Fe/Mn oxides).^c Oxidizable fraction (bound to organic matter and sulfides).^d Residual fraction (*aqua regia*).^e The values in parentheses are ratio of each extract to sum of each extraction.

soluble fractions of Cd, Pb, and Zn were 22.5 mg/kg (27.2%), 1,395 mg/kg (18.6%), and 1,095 mg/kg (22.8%), respectively.

3.2. The Change in the pH and EC Values of the Leachate.

Figure 2 shows the pH and EC (electrical conductivity) values of the leachate collected during the test period. The lowest pH was obtained from the leachate extracted from 1 PV by applying the initial aqueous solution of pH 5.6. The pH of the limestone-treated soil column was 7.4 and was higher than that of the control column, which was 6.8. Thereafter, the pH value abruptly increased and remained constant. When the acid solutions of pH 4.8 and pH 3.6 were added to the top of the soil layer at 11 PV and 21 PV, respectively, the pH values of leachates at 11 PV and 21 PV abruptly decreased, in a similar pattern to the early stage after the addition of the pH 5.6 solution (Figure 2(a)). In particular, the pH values decreased most abruptly directly after the inflow of the pH 4.8 solution

(at 11 PV) and were the lowest since the inflow at 1 PV. In the control soil, the pH temporarily decreased in the early stages of augmentation but increased again and remained constant thereafter. This seems to be in response to the natural buffering capacity of the soil, which included a large quantity of limestone, as mentioned earlier [20]. The limestone-treated soil showed a similar tendency to the control soil, and the pH was similar to that of the control soil after 1 PV. The decrease in the pH values after the initial inflow of the solutions, however, was significantly smaller than that in the control soil.

The EC of the leachate had the opposite tendency to that of the pH. The correlation between the pH and EC of the leachate was strongly negative ($r = -0.758$, with $P < 0.01$ and $n = 30$). At 1 PV, which had the lowest pH value within the test period, the EC value was highest, but it abruptly decreased when the pH 5.6 solution was added to the column (Figure 2(b)). In both the control and the limestone-treated soil columns, the EC abruptly increased at 11 and 21 PV, immediately after the inflow of the pH 4.8 and pH 3.6 solutions, respectively, and remained constant thereafter (Figure 2(b)).

The changes in the pH and EC values suggest that a large quantity of metal cations was initially leached after the inflow of acid solutions, when the pH decreased and the EC increased temporarily.

3.3. Leaching Concentrations of Heavy Metals in the Soil.

During the column test, the change in metal concentrations was observed from collected leachates of the control and limestone-treated columns. In the control soil, the Cd concentration in leachate was 81.9 $\mu\text{g/L}$ (the highest level during whole test period) at 1 PV, when the pH 5.6 solution was first applied to the soil column (Figure 3(a)). This level was eight times greater than the national limit of groundwater quality (10 $\mu\text{g/L}$) [23]. The concentration at 2 PV decreased to 25.6 $\mu\text{g/L}$, two times greater than the national limit. Cd concentration abruptly decreased thereafter and remained constant at a value below the national limit. Cd concentration abruptly decreased thereafter and remained constant at a value below the national limit. Cd concentration sharply increased again in the early stages after the addition of the pH 4.8 and pH 3.6 solutions. In particular, for the pH 4.8 solution, the Cd concentration at 11, 12, 13, and 14 PV exceeded the national limit. These results suggest that should this kind of site experience acidic rainfall, metals could be released to the surrounding environment at the early stage of rainfall, even though the pH value of soil used was higher than the reported value (pH 5.6) of farmland in South Korea [19].

In the column of limestone-treated soil, however, the Cd concentration was significantly lower than in the control soil and did not exceed the national limit. Moreover, it remained constant, unlike the case in the column of control soil, in which Cd was quickly leached during the early stages of the addition of an acid solution (Figure 3(a)). The total leached concentrations of Cd in the leachate were 8.40 $\mu\text{g/L}$ in the control column and 0.52 $\mu\text{g/L}$ in the limestone-treated column, which shows that the limestone treatment reduced the Cd concentration by approximately 94%.

Zn had almost the same leaching characteristics as Cd (Figure 3(b)). In the control column, the Zn concentration

FIGURE 2: Variation of the (a) pH and (b) EC values of the leachates from the soil columns.

FIGURE 3: Variation of the heavy metal concentrations in the leachates from the soil columns ((a) Cd; (b) Zn; and (c) Pb).

was 13,916 $\mu\text{g/L}$ and was approximately 14 times greater than the national limit of effluent quality of surface water of 1,000 $\mu\text{g/L}$. There is no national regulation of zinc in groundwater, so the surface water standards were used [23]. Zn concentrations from the control columns at 2 and 3 PV were 6,536 and 2,238 $\mu\text{g/L}$, respectively, which significantly exceeded the national limit. Thereafter, the Zn concentration continuously decreased to below the national limit. In the early stages of the addition of the pH 4.8 and pH 3.6 solutions, however, the Zn concentration abruptly increased again, in the same manner as for Cd. However, the Zn concentration increased quickly between 11 and 14 PV, which corresponded to the early stages of the addition of the pH 4.8 solution, and was maintained a little longer than Cd. The Zn concentrations at 12, 13, and 14 PV were 1,575, 2,144, and 2,548 $\mu\text{g/L}$, respectively, which exceeded the national limit. At 21 PV, the addition of the pH = 3.6 solution, the Zn concentration abruptly increased to 1,627 $\mu\text{g/L}$, which exceeded the national limit, and remained there for the rest of the test period.

In the limestone-treated column, the Zn concentration was significantly lower than that in the control column and remained below the national limit, without any obvious variation of leaching characteristics after the addition of acid solutions (Figure 3(b)). The total leached concentrations of Zn in the leachate were 1,832 $\mu\text{g/L}$ in the control column and 141 $\mu\text{g/L}$ in the limestone-treated column, which shows that the limestone treatment reduced the Zn concentration by approximately 92%. These results verify the obvious effect of limestone treatment to reduce the Zn concentration of column effluents.

The Pb concentration in the leachate was 9.9 $\mu\text{g/L}$ at 1 PV and abruptly decreased thereafter. As the pH 5.6 solution was being added, the Pb concentration remained constant at a level almost the same as that in the limestone-treated column (Figure 3(c)). At 11 PV, which corresponded to the addition of the pH 4.6 solution, the Pb concentration abruptly increased to 16.8 $\mu\text{g/L}$ and then decreased to a concentration similar to that in the limestone-treated column. At 20 PV, however, which was the final addition point of the pH 4.6 solution, the Pb concentration was 45.3 $\mu\text{g/L}$, the highest within the test period, and continued to increase as the pH 3.6 solution seeped into the soil.

In the limestone-treated column, the Pb concentration also increased somewhat abruptly at 11 and 20 PV but was significantly lower than in the control column. Under the pH 3.6 condition, the Pb concentration continued to increase in the control soil but remained constant at a significantly lower value (Figure 3(c)). The total leached concentrations of Pb in the leachate were 6.19 $\mu\text{g/L}$ in the control column and 1.31 $\mu\text{g/L}$ in the limestone-treated column, which showed that the limestone treatment reduced the Pb concentration by approximately 79%.

4. Discussion

In the control column, Cd, Zn, and Pb were quickly leached during the early stages of the inflow of the acid solutions (Figure 3), and the leached Cd and Zn concentrations initially exceeded the groundwater quality limit and the surface water

TABLE 5: Pearson's correlation coefficients r between Cd, Zn, Pb, and pH in leachates of control column ($n = 30$).

	pH	Cd	Zn	Pb
pH	1	-0.769**	-0.652**	0.038
Cd	-0.769**	1	0.965**	0.060
Zn	-0.652**	0.965**	1	0.069
Pb	0.038	0.060	0.069	1

* Significant at $P < 0.05$.

** Highly significant at $P < 0.01$.

standard, respectively, after the injection of the pH 5.6 and pH 4.6 solutions. During the supply of the pH 3.6 solution, the Zn concentration consistently exceeded the national limit of effluent quality of surface water in South Korea. The released Pb concentrations were relatively low, not exceeding the groundwater quality national limit of 100 $\mu\text{g/L}$, but abruptly increased after the addition of the pH 4.6 solution. The Pb concentration was highest at the final point of the addition of the pH 4.6 solution. The Pb concentration continued to rise as the pH 3.6 solution was added to the column.

The pH of the control column leachate initially decreased after the addition of the acid solutions (Figure 2), corresponding to the most abrupt increases in the Cd, Zn, and Pb concentrations (Figure 3). The correlation analysis of the pH and metal concentrations showed that Cd and Zn had a strongly negative correlation with pH (Table 5). As the soil contained a large quantity of limestone, its pH and acid buffering capacity were high, but its pH temporarily decreased directly after the addition of the acid solutions, leading to the abrupt leaching of its metal components.

The results of the column experiments described above showed that Cd, Zn, and Pb were also leached in the early stages of the experiment, after which their concentrations in the leachate continually decreased [24–29]. It is likely that the metals were present in highly soluble forms and immediately dissolved into the acid solutions and were leached [27]. Cd and Zn concentrations quickly increased after the inflow of the acid solutions and then quickly decreased. The pH of the leachate from the control column temporarily decreased directly after the supply of acid solutions and then abruptly increased due to the high alkalinity of the soil (Figure 2). An increase in pH enhances the negative charge on the soil, and the metal cations are adsorbed and precipitated onto the soil surface [14]. The affinity of metals for soil is enhanced more under neutral pH conditions than under acidic conditions because an increase in pH increases the electrostatic attraction of the materials adsorbed to the soil [30]. Therefore, it seems that Cd and Zn were quickly leached when the pH temporarily decreased, and then their concentrations in the leachate decreased as they were adsorbed or precipitated to the soil surface. It is expected, however, that the adsorbed and precipitated metals can easily be leached at any time with changes in rainfall and pH.

Leaching trends of Cd and Zn in the control column showed a strong positive correlation (Figure 3 and Table 5). Chemically, Cd and Zn are very similar and are known to

coexist in nature [31]. Cd and Zn within the control column, and the leachate of the present column test, displayed similar leaching trends. The leaching trends of Pb, however, did not show any significant correlation with Cd and Zn and instead showed characteristics that were different from those of Cd and Zn. Such correlation between Cd, Zn, and Pb in the leachate, or the leaching characteristic, was similar to the results described by Houben et al. [28].

The total Cd, Zn, and Pb contents were 90.8 mg/kg, 5,196 mg/kg, and 8,058 mg/kg, respectively, in the soil used (Table 3). The total Pb content was highest by a wide margin and was approximately 88 times greater than that of Cd (Table 3). The total leached concentrations were the sum of the metal concentrations in the leachate collected over the test period divided by the number of leachates sampled ($n = 30$). The total leached concentrations of Cd, Zn, and Pb were 8.40, 1,832, and 6.19 $\mu\text{g/L}$, respectively, with the Pb concentration being by far the lowest. Pb is the most stable component of all metals found in soils [32–34], and Zhang and Pu [24] reported that Pb has the lowest mobility in nonacidic soils. The results of sequential extraction analyses on metals from soil samples are shown in Table 4. The acid soluble fractions of Cd, Pb, and Zn were 22.5 mg/kg (27.2%), 1,395 mg/kg (18.6%), and 1,095 mg/kg (22.8%), respectively. Pb had a lower composition of weakly bound fractions than did Cd and Zn. The acid soluble fraction had the highest mobility and phytoavailability in soil. Kuo and Baker [35] and McLean and Bledsoe [36] suggest that Pb prevents the sorption of Cu and Zn in soil. Cu and Zn also prevent the sorption of Cd. Therefore, Pb has the highest preferential adsorption in soils.

These characteristics of Pb in soil can be used to explain why Pb displayed different leaching characteristics than did Cd and Zn. Moreover, these characteristics of Pb were more visible because of the high pH of the subject soil, which is due to the high content of limestone in the bedrock of the subject area.

The leached Pb concentration, however, was the highest at the final inflow point of the pH 4.8 solution and continued to increase as the pH 3.6 solution was being added to the soil. The concentration of Pb in the leachate collected during the observation period was below the national limit despite a high Pb content due to the characteristics of Pb, which has relatively lower mobility than other metals in soil. However, the fact that the average pH of general Korean farmlands is slightly acidic at $\text{pH} = 5.6$ shows that Pb can be greatly leached at concentrations that can affect the surrounding environment due to pH changes, such as acid rain.

In the limestone-treated column, the decrease in pH was significantly smaller than that in the control column, and abrupt leaching of metals was almost never observed. Unlike the control column, in which metal concentrations significantly exceeded the national limit, metal concentrations were much lower than the national limit in the limestone-treated column. The main component of limestone, CaCO_3 , is a representative proton acceptor [37], and it seems that the increase in CaCO_3 reduced H^+ and increased OH^- concentrations in the soil as the acid solutions passed through it, and the pH remained constant, even in the early stages of acid solution addition. Accordingly, it was believed that the

leached metal concentrations decreased significantly because the acid buffering capacity of the soil was maintained.

5. Conclusions

This study examined the release of metals, especially Cd, Zn, and Pb, from contaminated soil treated by limestone, using a laboratory-scale column test with varying pH. pH values were restricted to 3.6, 4.8, and 5.6. In this study, the pH of the subject soil was significantly high despite being from farrow land. This soil characteristic was not anticipated when this study was planned. Limestone was selected as the stabilization agent to reduce metal mobility by increasing soil pH because most Korean farmlands are slightly acidic. The characteristics of the treatment process of the stabilization method make determining an appropriate stabilization agent the most important task. If the pH of the soil in the reclamation target area is too high, the range of stabilization agents that can be selected narrows as generally alkaline material is not considered as a stabilization agent. However, this study generated some interesting results, which might provide basic data that can be considered when applying stabilization methods to contaminated soil with high pH for reclamation. Furthermore, highly alkaline soil can rapidly leach metal at high concentrations when rain or acidic rains temporarily reduce the acid buffering capacity of the soil. Slightly acidic soil was predicted to have noticeable effects on the mobility of metals and on the surrounding water systems induced by normal rain. Applying a stabilization agent such as limestone, however, was found to effectively reduce the leaching of metals by continuously maintaining the acid buffering capacity of the soil under conditions of altered pH such as acid rain. Moreover, despite the subject soil exhibiting a high pH, limestone treatment did not increase the pH in a way that was disadvantageous to the soil environment.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

The authors are thankful to the Korean Mine Reclamation Corp. (<http://www.mireco.or.kr/>), Seoul, Korea, for financial support.

References

- [1] B.-Y. Park, J.-K. Lee, H.-M. Ro, and Y. H. Kim, "Effects of heavy metal contamination from an abandoned mine on nematode community structure as an indicator of soil ecosystem health," *Applied Soil Ecology*, vol. 51, no. 1, pp. 17–24, 2011.
- [2] MIRECO, *Yearbook of MIRECO Statistics 2009*, Mine Reclamation Corporation, Seoul, Republic of Korea, 2010.
- [3] Y. S. Ok, A. R. A. Usman, S. S. Lee et al., "Effects of rapeseed residue on lead and cadmium availability and uptake by rice plants in heavy metal contaminated paddy soil," *Chemosphere*, vol. 85, no. 4, pp. 677–682, 2011.

- [4] R. Khan, S. H. Israili, H. Ahmad, and A. Mohan, "Heavy metal pollution assessment in surface water bodies and its suitability for irrigation around the Neyevli lignite mines and associated industrial complex, Tamil Nadu, India," *Mine Water and the Environment*, vol. 24, no. 3, pp. 155–161, 2005.
- [5] Y. M. Wang, T. C. Chen, K. J. Yeh, and M. F. Shue, "Stabilization of an elevated heavy metal contaminated site," *Journal of Hazardous Materials*, vol. 88, no. 1, pp. 63–74, 2001.
- [6] A. Ruttens, K. Adriaenssens, E. Meers et al., "Long-term sustainability of metal immobilization by soil amendments: cyclonic ashes versus lime addition," *Environmental Pollution*, vol. 158, no. 5, pp. 1428–1434, 2010.
- [7] N. T. Basta and S. L. McGowen, "Evaluation of chemical immobilization treatments for reducing heavy metal transport in a smelter-contaminated soil," *Environmental Pollution*, vol. 127, no. 1, pp. 73–82, 2004.
- [8] W. Hartley, R. Edwards, and N. W. Lepp, "Arsenic and heavy metal mobility in iron oxide-amended contaminated soils as evaluated by short-and long-term leaching tests," *Environmental Pollution*, vol. 131, no. 3, pp. 495–504, 2004.
- [9] M. Malandrino, O. Abollino, S. Buoso, A. Giacomino, C. La Gioia, and E. Mentasti, "Accumulation of heavy metals from contaminated soil to plants and evaluation of soil remediation by vermiculite," *Chemosphere*, vol. 82, no. 2, pp. 169–178, 2011.
- [10] J. Kumpiene, A. Lagerkvist, and C. Maurice, "Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments—a review," *Waste Management*, vol. 28, no. 1, pp. 215–225, 2008.
- [11] H. M. Conesa, Á. Faz, and R. Arnaldos, "Heavy metal accumulation and tolerance in plants from mine tailings of the semiarid Cartagena-La Unión mining district (SE Spain)," *Science of the Total Environment*, vol. 366, no. 1, pp. 1–11, 2006.
- [12] Korea Ministry of Environment, *Investigation of Soil Pollution Status Nearby Abandoned Metal Mine*, Ministry of Environment, Gwacheon, Republic of Korea, 2007.
- [13] Korea Ministry of Environment, *Standard Methods of Soil Sampling and Analysis*, Ministry of Environment, Gwacheon, Republic of Korea, 2009.
- [14] C. Appel and L. Ma, "Concentration, pH, and surface charge effects on cadmium and lead sorption in three tropical soils," *Journal of Environmental Quality*, vol. 31, no. 2, pp. 581–589, 2002.
- [15] Mine Reclamation Corporation (MIRECO), *Monitoring on Heavy Metal Behavior in Remediated Area*, Technology Series 2012–81, Mine Reclamation Corporation (MIRECO), Seoul, Republic of Korea, 2012, http://www.mireco.or.kr/jsp/bbs_template/front/data06/download.csp?wid=NW03050101&idx=1358905353891.
- [16] Korea Ministry of Environment, "Annual report of ambient air quality in Korea 2006," Tech. Rep., Korea Ministry of Environment, Gwacheon, Republic of Korea, 2007.
- [17] NIST, *Methods of Soil Chemical Analysis*, National Institute of Agricultural Science and Technology, RDA, Suwon, Republic of Korea, 2000.
- [18] Korea Ministry of Environment, *Standard Methods of Water Sampling and Analysis*, Ministry of Environment, Gwacheon, Republic of Korea, 2009.
- [19] B. Jung, J. Choi, E. Yun, J. Yoon, and Y. Kim, "Monitoring on chemical properties of bench marked upland soils in Korea," *Korean Journal of Soil Science and Fertilizer*, vol. 34, no. 5, pp. 326–332, 2001.
- [20] E. H. Hwang, *A study on the heavy metal contamination of paddy soil in the vicinity of the Seosung Pb-Zn mine [M.S. thesis]*, Korea National University of Education, Gangnae-Myeon, Republic of Korea, 2000.
- [21] J.-M. Lee, W.-R. Go, A. Kunhikrishnan et al., "Model development for estimating total arsenic contents with chemical properties and extractable heavy metal contents in paddy soils," *Korean Journal of Soil Science and Fertilizer*, vol. 45, no. 6, pp. 920–924, 2012 (Korean).
- [22] Korea Ministry of Environment, *Soil Environment Conservation Act*, Ministry of Environment, Gwacheon, Korea, 2010.
- [23] Korea Ministry of Environment, *Water Quality Conservation Act*, Ministry of Environment, Gwacheon, Republic of Korea, 2010.
- [24] M. Zhang and J. Pu, "Mineral materials as feasible amendments to stabilize heavy metals in polluted urban soils," *Journal of Environmental Sciences*, vol. 23, no. 4, pp. 607–615, 2011.
- [25] P. Schwab, D. Zhu, and M. K. Banks, "Heavy metal leaching from mine tailings as affected by organic amendments," *Biore-source Technology*, vol. 98, no. 15, pp. 2935–2941, 2007.
- [26] S. Hu, X. Chen, J. Shi, Y. Chen, and Q. Lin, "Particle-facilitated lead and arsenic transport in abandoned mine sites soil influenced by simulated acid rain," *Chemosphere*, vol. 71, no. 11, pp. 2091–2097, 2008.
- [27] J. W. Jeon, B. H. Bae, and Y. H. Kim, "Applicability test of various stabilizers for heavy metals contaminated soil from smelter area," *Korean Geo-Environmental Society*, vol. 11, pp. 63–75, 2010.
- [28] D. Houben, J. Pircar, and P. Sonnet, "Heavy metal immobilization by cost-effective amendments in a contaminated soil: effects on metal leaching and phytoavailability," *Journal of Geochemical Exploration*, vol. 123, pp. 87–94, 2012.
- [29] P. Hu, B. Yang, C. Dong et al., "Assessment of EDTA heap leaching of an agricultural soil highly contaminated with heavy metals," *Chemosphere*, vol. 117, pp. 532–537, 2014.
- [30] R. Naidu, R. S. Kookana, M. E. Sumner, R. D. Harter, and K. G. Tiller, "Cadmium sorption and transport in variable charge soils: a review," *Journal of Environmental Quality*, vol. 26, no. 3, pp. 602–617, 1997.
- [31] K. W. Smilde, B. van Luit, and W. van Driel, "The extraction by soil and absorption by plants of applied zinc and cadmium," *Plant and Soil*, vol. 143, no. 2, pp. 233–238, 1992.
- [32] M. Pueyo, J. Sastre, E. Hernandez, M. Vidal, J. López-Sánchez, and G. Rauret, "Prediction of trace element mobility in contaminated soils by sequential extraction," *Journal of Environmental Quality*, vol. 32, no. 6, pp. 2054–2066, 2003.
- [33] L. Ramos, L. M. Hernandez, and M. J. Gonzalez, "Sequential fractionation of copper, lead, cadmium and zinc in soils from or near Donana National Park," *Journal of Environmental Quality*, vol. 23, no. 1, pp. 50–57, 1994.
- [34] S. M. Ullrich, M. H. Ramsey, and E. Helios-Rybicka, "Total and exchangeable concentrations of heavy metals in soils near Bytom, an area of Pb/Zn mining and smelting in Upper Silesia, Poland," *Applied Geochemistry*, vol. 14, no. 2, pp. 187–196, 1999.
- [35] S. Kuo and A. S. Baker, "Sorption of copper, zinc, and cadmium by some acid soils," *Soil Science Society of America Journal*, vol. 44, no. 5, pp. 969–974, 1980.
- [36] J. E. McLean and B. E. Bledsoe, "Behavior of metals in soils," in *EPA Environmental Assessment Sourcebook*, p. 19, 1996.
- [37] A. Aiuppa, P. Bonfanti, and W. D'Alessandro, "Rainwater chemistry at Mt. Etna (Italy): natural and anthropogenic sources of major ions," *Journal of Atmospheric Chemistry*, vol. 46, no. 1, pp. 89–102, 2003.