

Stabilization of Metals-contaminated Farmland Soil using Limestone and Steel Refining Slag

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ABSTRACT

The metals contamination of farmland soil nearby abandoned metal mine was serious problem in Korea. Stabilization of contaminated soil was reported using various stabilizers. Application of limestone and steel refining slag was reported as effective stabilizers in the stabilization of metals. The batch studies confirmed that the mixture of limestone and steel refining slag was suitable for stabilization of metals in contaminated soil. The limestone and steel refining slag mixture (2 : 1 and 3 : 2) were used in column studies and it was confirmed that the stabilizers effectively stabilized heavy metals in contaminated soil. The pH of the soil was increased with the addition of stabilizers. Total leached concentration of metals from the column study was reduced 44, 17, and 93% in comparison to the control at arsenic, cadmium and copper, respectively. The sequential extraction studies showed that the exchangeable fraction was changed into carbonate bound fraction (Cd and Cu) and Fe-Mn oxide bound fraction (As). Based on the results we confirmed that 2:1 ratio of limestone and steel refining slag effectively stabilizes the heavy metals. The mixed treatment of lime stone with steel refining slag would be an effective and feasible method for controlling metals leaching in contaminated soil.

Key words : Abandoned mine, Stabilization, Sequential extraction, Limestone, Steel refining slag

1. Introduction

The contamination of metals in Korean farmlands was caused by various anthropogenic factors. During the past few decades, environmental problems caused by metal pollution from mining activities have received increasing attention. Metals contamination of farmland soil nearby abandoned metal mines was very serious in Korea (MOE, 2009a). According to Mine Reclamation Corporation in Korea, 6037 mines are located in Korea which includes 391 coal mines, 3538 nonmetallic mines and 2108 metallic mines (Mireco, 2009). More than 80% of these mines are now closed and these mines cause several environmental pollution during long times. Furthermore mining and refining installation of abandoned metal mines were neglected in ruin. Also mine tailing and ore rock waste were scattered without control (Kim et al., 2002). Mine tailings and waste-

water are the major sources of metal pollution into the environment. The high concentrations of metals in the environment have detrimental effects on chemical and biological properties of soil (Lothenbach et al., 1999). These toxic metals can eventually harm to plants and health of human through the food chain (Ok et al., 2007). Most tailings and mine wastes are remained on slopes and contaminate nearby agriculture soil and streams (Yang et al., 2006). According to the Korean Soil Environmental Conservation Act (KSECA), metals concentration of farmland soils was restricted with arsenic, cadmium, copper, lead, and zinc at a concentration of 25, 200, 4, 150 and 300 mg/kg, respectively. Thus, it should be monitored continuously and restricted from agricultural usage.

Solidification and stabilization used for treatment of metal contaminated soil. These process are applicable to both in-situ and ex-situ remediation. It has low cost and

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short treatment period. Thus solidification or stabilization have been considered as available and effective option for treatment of metal contaminated farmland soils nearby abandoned metals mines (Lee, 2007). Solidification is reducing the mobility of contaminants using solidifying agents and stabilization is reducing the toxicity, solubility and mobility by changing the state of contaminants. In treatment of farmland soils nearby abandoned metal mines, stabilization is more widely used than solidification (Kim, 2010). Numerous studies reported the application of various stabilizers to treat different contaminants. Also many stabilizers were used for assessment of stabilization of arsenic and heavy metals (Kumpiene et al., 2008). The mechanisms of stabilization of heavy metals in contaminated soil are absorption, precipitation, ion exchange (Park et al., 2010). It has been established that various factors such as pH, diameter, moisture content, concentration and form of heavy metals and transmissibility highly influence the metals stabilization in soil, but the most important factor is types of stabilizer on various contaminants in soil (Kumpiene et al., 2008). The mobility and leachability of cation heavy metals in contaminated soil was reduced through precipitation and insolubilization via increasing of pH (Kaasalainen and Yli-Halla, 2003). The various limes are typical material to reduce of leachability of heavy metals through increase in soil pH (Lee et al., 2007). However the high pH causes the increasing of mobility and toxicity of arsenic. Thus, arsenic treatment is difficult in high pH value (Hartley et al., 2004). In previously study, iron oxides

was used as effective materials for reducing of mobility of arsenics in high pH value. Iron oxides made complex with arsenic in soil, such as $\text{FeAsO}_4 \cdot \text{H}_2\text{O}$ or $\text{Fe}_3(\text{AsO}_4)_2$ (Kim et al., 2003).

The objectives of this study were to (i) assess the possibility of stabilization of contaminated farmland soil nearby abandoned metals with limestone and steel refining slag, and (ii) provide optimum ratio of stabilizers for stabilization of contaminated soil. This study is important because the soil site of this study used to farming now, it will cause the problem in various organisms include human and animals.

2. Materials and Methods

2.1. Soil sample collection and analysis

Soil was collected from paddy farmlands around the mine sites located in Masan of Gyeong-nam province in South Korea. The geographical information of the sampling site is shown in Fig. 1. This mine was a major source and supply of Cu on 1970s. The soil was collected from both top (15 cm from the ground surface) and sub (50 cm from the ground surface) regions. After air-drying at room temperature for 1 week, samples were disaggregated and sieved into a 10 mesh (less than 2 mm). Physicochemical properties of the soil were analyzed according to Korean standard analysis for soils (MOE, 2009b). The concentration of heavy metals in soil was analyzed using sequential extraction method (Tessier et al., 1979). Sequential extraction studies reported the availability, mobilization, and transport of trace

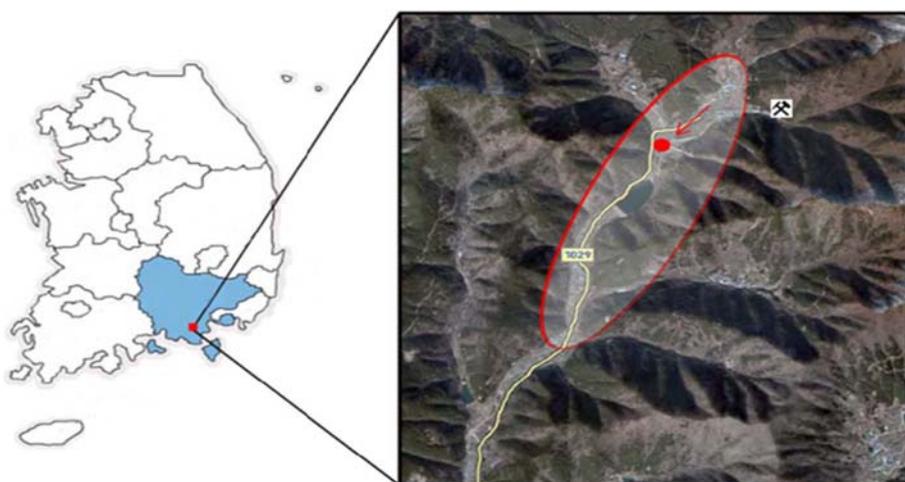


Fig. 1. Location of sampling site in South Korea (Latitude; 35° 11' 22", Longitude; 126° 23' 16").

of metals and metalloids. Sequential extraction procedure reveals five types of metal binding mechanisms in soil such as, 1) species associated with the exchangeable phase, 2) species associated with the acid soluble phase such as carbonate and acid rain, 3) species adsorbed onto solid particles such as iron and manganese oxides, 4) species associated with oxidizable organic matter, 5) residual fraction with mineral matter. The first and second fractions were considered to easily leach through change of natural conditions.

2.2. Characterization of lime stone and steel refining slag

In this study, limestone (LS) was used to increase the soil pH and to reduce the mobility and leachability of metals in the soil. Steel refining slag (SRS) was used to remove arsenic in the soil. The iron oxide present in SRS seems to be effective in arsenic treatment. The LS and SRS were provided from Deaseong MDI and Ecomaister in the Korea, respectively. The composition of the stabilizers was analyzed by using X-ray fluorescence spectrometer (XRF; Axios minerals, PANalytical, Netherlands). The stabilizers were sieved into a 10 mesh (less than 2 mm) and used for further experiments.

2.3. The batch test for collection of stabilizer ratio

Batch studies were conducted to optimize the effective ratio of stabilizers. The addition ratio of LS (1, 3 and 5%), SRS (1, 3 and 5%) and LS : SRS (1 : 1, 2 : 1, 2 : 3 and 3 : 2) was used for the studies. The ratio of stabilizers was calculated as a percentage of the total soil (20 g). Briefly, 20 g of soil with calculated stabilizers was dispensed in 250 mL Erlenmeyer flask containing 100 mL of distilled water. The flasks were incubated at room temperature for 36 h. Samples were collected at predetermined time intervals (0.5, 1, 2, 4, 6, 12 and 36 h) and centrifuged at 13,000 rpm for 20 min. The supernatant was used for metal analysis using inductively coupled plasma-atomic emission spectrophotometry (ICP-AES; Leeman Labs, Inc., Hudson, NH, USA). Commercially available stock solutions were used to prepare appropriate elemental calibration standards for the ICP-AES. Analysis of sample and standard solutions was based on the mean of three readings. Solutions of HNO_3 were used as reagent blanks. To check analytical quality, a

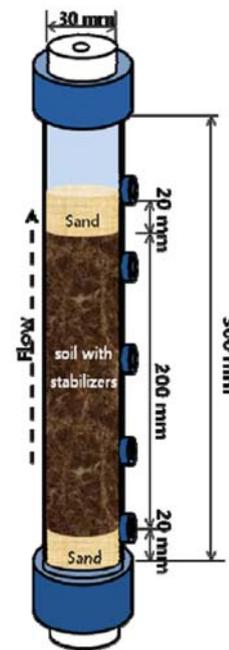


Fig. 2. The diagram of the used column in this study.

rigorous quality control program was implemented, which included reagent blanks, triplicate samples and certified international materials (BCR-701) (Ramsey et al, 1987). The precision and bias of the chemical analysis was less than 10%.

2.4. Continuous column experiment for comparison of leaching concentration from soil

A glass column including capping plates, valves and tube was used (30 cm length \times 3.0 cm in diameter). The bottom part of the column (2 cm) was filled with sand, later it was filled with soil and stabilizers (20 cm), and again filled with sand (2 cm) (Fig. 2). The ratio of stabilizer in each column was selected from the results of batch tests. Thus two type of ratio (LS : SRS; 2 : 1 and 3 : 2) was selected for the stabilization of contaminated soils. The pH of the used water was adjusted 5.6 for the same as the pH of acid rains using NaOH and H_2SO_4 solution. A flow speed of water in column was adjusted into 1 pore volume/day. The soil has 1.52, 1.56 and 1.62 g/cm^3 of dry unit weight at control, 2 : 1 and 3 : 2 columns. The pore volume has 0.35, 0.31 and 0.3 L at control, 2 : 1 and 3 : 2 columns. The direction of flow was upward from the bottom of column (Fig. 2). Samples were collected every 24 h of the cycle and centrifuged

at 13,000 rpm for 20 min. The supernatant was used for analysis of metals. The samples were collected a total of 15 times and metal distribution in the soil was measured using sequential extraction methods.

3. Results and discussion

3.1. Characteristics of contaminated soil and stabilizers

The physicochemical characteristics of contaminated soil are represented in Table 1. The pH of the soil was 6.2, this pH value is slightly higher than pH 5.6 which is an average of Korean soil pH value (Jung et al., 2001). The EC, CEC, organic carbon and total organic matter of the soil were 8.83 $\mu\text{s}/\text{cm}$, 2.66 cmol^+/kg , 1.47%, and 2.53%, respectively. However, the concentrations of arsenic and other heavy metals were exceeded the criteria set by The Korean Soil Environment Conservation Act (SECA) (Table 2). Arsenic, cadmium and copper were higher than Anxiety Criterion level. Especially, copper was exceeded the Countermeasure criterion, it shows the soil was significantly contaminated

Table 1. Physical and chemical properties of contaminated soils

Environmental variable	Soil sample
pH	6.21
Electric conductivity ($\mu\text{s}/\text{cm}$)	8.83
Cation exchange capacity (cmol^+/kg)	2.66
Organic carbon (%)	1.47
Total organic Matter (%)	2.53

Table 2. Total metal concentrations in contaminated soils

		As	Cd	Cu	Pb	Zn
SECA ¹⁾	AC ²⁾	25	4	150	200	300
	CC ³⁾	75	12	450	600	900
Concentration (mg/kg)		37.9	5.97	604.4	21.9	116.0

¹⁾ Korean Soil Environmental Conservation Act. (SECA)

²⁾ Anxiety Criterion

³⁾ Countermeasure Criterion

Table 3. Chemical composition of medias

Size (mm)	Content (%)									
	CaO	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	MnO	CO ₂	
LS	2-6	53.24	2.38	0.45	0.84	0.2	–	0.13	1.35	40.28
SRS	1-5	30.6	12.4	7.08	3.05	28.1	0.51	0.28	5.77	–

with copper. Based on the XRF analysis we found that the chemical compound present in LS was CaO (53.24%), CO₂ (40.28%) and SiO₂ (2.38%). Also SRS was CaO (30.6%), SiO₂ (12.4%), and F₂O₃ (28.1%) (Table 3).

3.2. Batch studies for the selection of stabilizers ratio

The effective ratios of LS and SRS for the stabilization of metal were determined using batch studies. The control soil without LS and SRS showed pH 6.21. However, the addition of LS (1, 3 and 5%) significantly increased the pH to 7.08, 7.51 and 7.67, respectively. The leaching of arsenic was increased according to LS concentration. Maximum arsenic leaching 1026 $\mu\text{g}/\text{L}$ was observed at 5% LS. However, leaching of other metals decreased according to

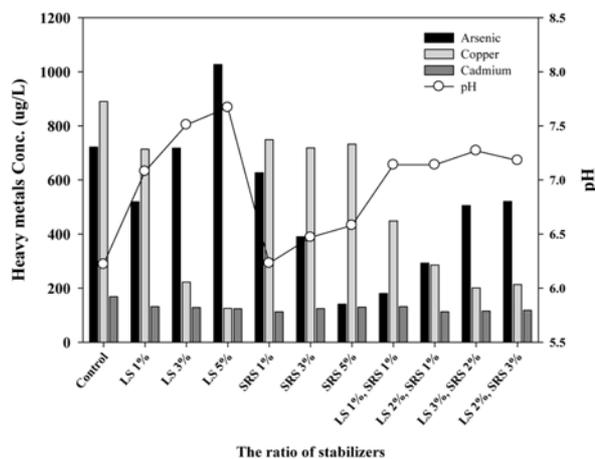


Fig. 3. The results of batch test that stabilization of contaminated soil for selection of stabilizer ratio.

increasing LS concentration. Copper leaching was significantly decreased than control soil, whereas cadmium leaching was slightly decreased than control soil. SRS was not so effective in changing the pH compared with LS. The pH of LS : SRS (1 : 1, 2 : 1, 3 : 2 and 2 : 3) was confirmed at around 7.1 (pH 7.14~7.27). The leaching of arsenic was significantly decreased according to the concentration of SRS. However, copper leaching was slightly reduced and cadmium leaching was slightly increased by SRS. In LS:SRS applied soil, leaching of arsenic was increased according to the concentration of LS. The results are similar to that of LS stabilizer. However, the amount of leached arsenic was low compared with LS alone. Leaching of copper was reduced according to increasing LS concentration. However, concentration of leached cadmium has similar to LS : SRS applied soil. The negative charge on the soil colloids in nearly neutral or alkaline pH enhances the adsorption of cationic metals towards soil colloids (Bolan et al., 2003). The arsenic is stabilized through formation of insoluble iron-arsenic compounds with SRS (Kim et al., 2003). The results indicate that the ratio (2 : 1) of LS and SRS was most suitable for the stabilization of arsenic, cadmium, and copper.

3.3. Study of effective ratio of stabilizers by column study

The ratio of stabilizers used in column study was selected by batch test that stabilizes arsenic, cadmium and copper (Fig. 4). The optimum ratio of the stabilizers (LS : SRS) were determined that 2 : 1 and 3 : 2 from batch test. The leaching of arsenic was highly decreased than other metals. The arsenic concentration was not exceeded 50 $\mu\text{g/L}$, a quality standard of ground water (MOE, 2010). However, in control it was exceeded one time at 13th day. The leaching of cadmium was generally low after the addition of stabilizers. Similarly, leaching of copper in the control was higher than the stabilizer treated soil. However, the concentration of cadmium and copper is below the quality standard of ground water of Korea (MOE, 2010) (Table 4). The increased pH was observed by the addition of stabilizers. Addition of LS : SRS ratio 2 : 3 was increased the soil pH up to 7.6. The LS : SRS ratio 2 : 1 was effective than 3 : 2 for arsenic stabilization, whereas LS : SRS ratio 3 : 2 was effective for stabilizing the metals in contaminated farmland soil.

Total leached concentration of arsenic and other heavy metals are shown in Fig. 5. The results showed that the control has highest leaching concentration of arsenic and other

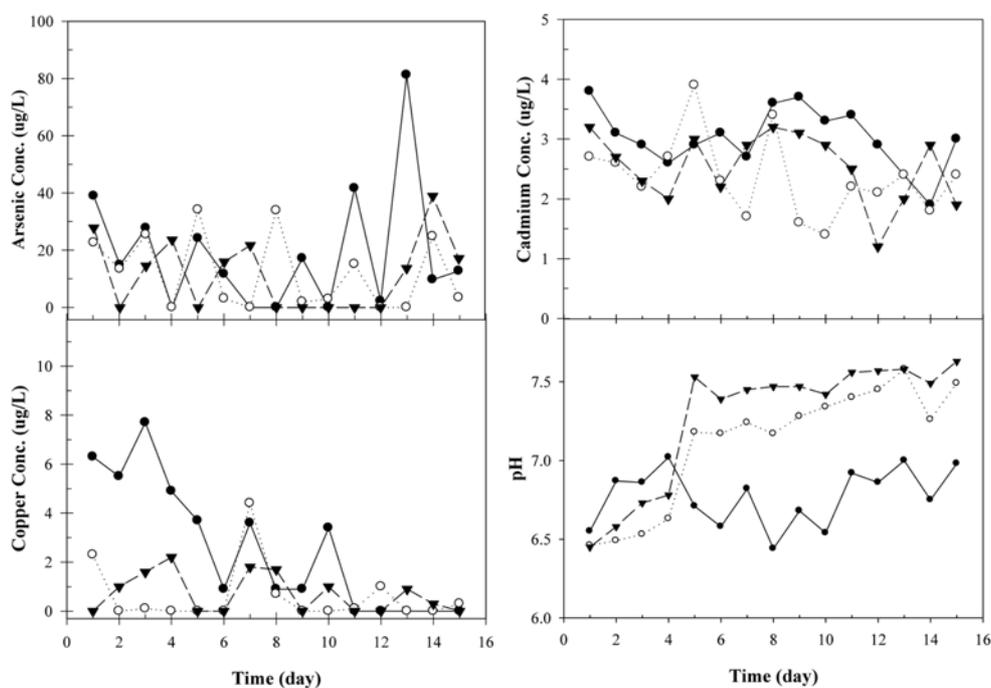


Fig. 4. The results of Column test for selection of optimum stabilizer ratio. Without treat (●), Addition of Limestone : Steel refining slag; 2 : 1(○), 3 : 2(▼).

Table 4. Precautionary value of Quality standard of ground water

Metals	Precautionary value (mg/L)
Arsenic	0.05
Cadmium	0.01
Lead	0.1

*Copper is not content of Act

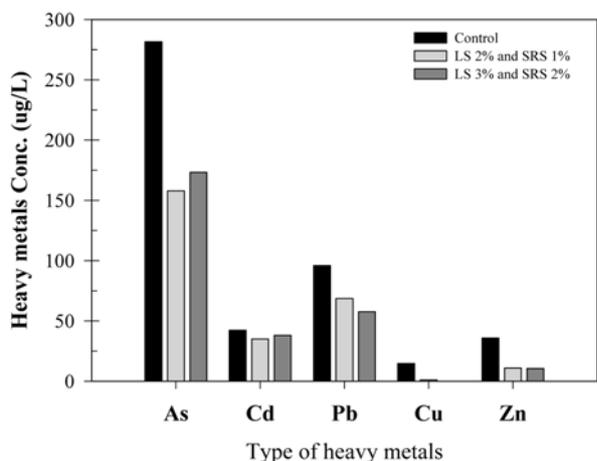


Fig. 5. The total leached concentration of arsenic and heavy metals in column test for selection of optimum stabilizer ratio.

heavy metals. Also, arsenic concentration in non treated soil was 281 $\mu\text{g/L}$ in 15 days. However, stabilizers (LS with SRS) treatment showed 157.9 $\mu\text{g/L}$ (43.9% reduction in comparison to the control) of arsenic for 2 : 1 ratio of stabilizers and 173 $\mu\text{g/L}$ (38.5% reduction in comparison to the control) of arsenic for 3:2 ratio of stabilizers. Similarly, the concentration of leached cadmium from LS:SRS ratio 3 : 2 was lower than LS : SRS ratio 2 : 1. However, the leached copper and lead from LS : SRS ratio 2 : 1 was lower than LS : SRS ratio 3 : 2. The leached copper was significantly

decreased 93.2, 97.2% in comparison to the control at 2 : 1 and 3 : 2, respectively. The leaching of zinc has similar tendency on both the ratios of stabilizers. The results suggested that the addition of 2% LS with 1% SRS was suitable in stabilization of contaminated soil with arsenic and other heavy metals. Also, the stabilizer may not have major influence on the soil pH. The results indicated that the treatment of LS 2% with SRS 1% was considered the most suitable ratio for farmland soil contaminated soil. In this study, the leaching rate of arsenic was decreased by 43.9% in 2 : 1 of LS:SRS ratio and 38.5% in 3 : 2 of LS : SRS ratio, respectively. The results corroborate with previous studies (Yun et al., 2011) in which leaching rate of arsenic decreased by 32.2% in SRS (5%) and 28.1% in LS (3%) compared to control. In case of copper, the leaching rate was decreased of 93.2% in 2 : 1 of LS:SRS ratio and 97.2% in 3 : 2 of LS : SRS, respectively. The results are in agreement with previous studies (Gray et al., 2006), outlined leaching of copper decreased 83.7 % in added lime in comparison to the control. However, stabilization of heavy metals by leaching shows different tendencies depending upon soil characteristics and concentration of contaminants.

3.4. Sequential extraction

The sequential extraction was suitable analysis to assess the effectiveness of soil stabilization with stabilizers. After stabilization process, change in fractions 1 to 5 indicates the effectiveness of stabilization. The exchangeable fraction of arsenic determined that 7.4% of the total content (Fig. 6). Exchangeable fraction is important factor in type of fraction, because this fraction is easily exchange with other ion

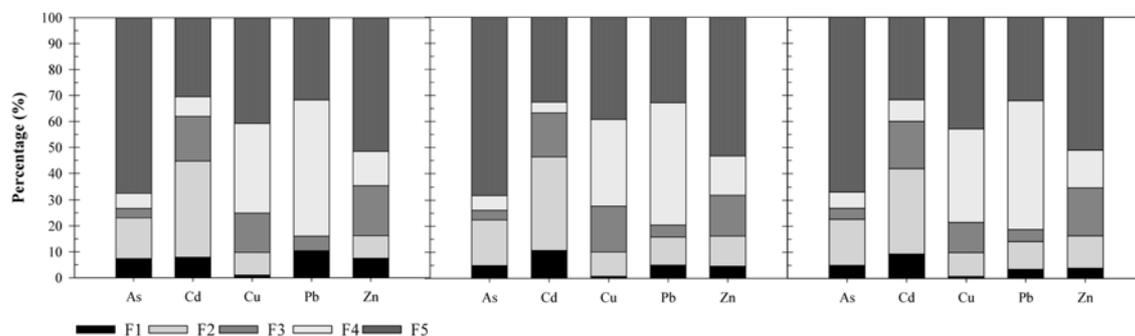


Fig. 6. The sequential extraction of soil which before (A) treatment and after with Lime stone: Steel refining slag; 2 : 1 (B), 3 : 2 (C). F1: exchangeable; F2: bound to carbonates (acido-soluble); F3: bound to Fe-Mn oxides (reducible); F4: bound to organic matter (oxidizable); F5: Residuals.

present in soil particles or changing of pH condition. It has been reported that the exchangeable fraction was important factor in contaminating the ground water and accumulation into plants (Shin, 2003). The exchangeable fraction of arsenic was effectively reduced on 4.9 and 5.0% by addition of LS : SRS ratio 1 : 2 and 3 : 2, respectively. The reducible fraction was less increased from 3.6 to 4.3%. Kim et al. reported that the exchangeable fraction of arsenic precipitate with iron from steel refining slags (Kim et al. 2003). This precipitation of arsenic was more stabilized than exchangeable fraction. The Fe-Mn oxide fraction of copper was slightly increase by addition of stabilizers and the exchangeable fraction of copper was almost changed to other fraction. The exchangeable fractions of lead and zinc fraction has been changed to bound to carbonate (acid-soluble) fraction. The cadmium fraction in soil confirmed that exchangeable fraction has 7.9%. This result indicates slightly high percentage than arsenic, copper and zinc of exchangeable fraction. It was same tendency with previously study that cadmium in contaminated soil of nearby abandoned mine has high percentage of exchangeable fraction (Ullrich et al., 1999). Exchangeable fraction of 2% LS and 1% SRS slightly increased than untreated soil. In this study, the results of fraction percentage was slightly changed than previously study (Jeong and NamKoong, 2013), however the leaching of metals in stabilized soil certainly reduced than control soils.

4. Conclusion

The present study focused on the selection of effective stabilizer ratio for the stabilization of contaminated farmland soil nearby abandoned mine with arsenic and other heavy metals using LS and SRS. Column study was conducted for the selection of effective stabilizer ratios. Sequential extraction studies indicate that the addition of stabilizers reduced the exchangeable fractions of metals. The batch study for the selection of suitable ratio of stabilizer was indicated that treatment of LS led to increase the soil pH and arsenic leaching. Treatment of SRS showed decreased concentration of arsenic leaching however, it has low stabilizing tendency at metal stabilization. The mixed treatment of LS and SRS (ratio of 2 : 1 and 3 : 2) has great stabilizing

tendency in both arsenic and other heavy metals stabilization. However, the mixed treatment of LS and SRS has effective removal efficiency. In conclusion, stabilization of metals using precipitation process should consider a suitable pH condition because leaching of arsenic is increased at high pH. According to this study, the suitable pH was confirmed as 7.2. The addition of LS 2% with SRS 1% is suitable in stabilization of soils. The leached metals in addition of LS 2% with SRS 1% decreased 43.9, 17.3 and 93.2% in comparison to the control at arsenic, cadmium and copper, respectively. Our study clearly demonstrated that the LS and SRS were effectively stabilized the arsenic and other heavy metals in the soil. Furthermore, this study needs a monitoring for long times because stabilizers need suitable times to interaction with metals and soils.

References

- Bolan, N.S., Adriano, D.C., and Curtin, D., 2003, Soil acidification and liming interactions with nutrient and heavy metal transformation and bioavailability. *Adv. in Agorn*, **8**, 215-272.
- Gray, C.W., Dunham, S.J., Dennis, P.G., Zhao, F.J., and McGrath, S.P., Field evaluation of in situ remediation of a heavy metal contaminated soil using lime and red-mud, *Environmental Pollut.*, **142**, 530-539.
- Hartley, W., Edwards, R., and Lepp, N.W., 2004, Arsenic and heavy metal mobility in iron oxideamended contaminated soils as evaluated by short-and long-term leaching tests, *Environ. Pollut.*, **131**, 495-504.
- Jeong, T.H. and Namkoong, W., 2013, Comparison of effect of two different amendments on immobilization of heavy metals in soil, *J. of Korea Society of Waste Management*, **30**, 408-417.
- Jung, B.G., Choi, J.W., Yun, E.S., Yoon, J.H., and Kim. Y.H., 2001, Monitoring on chemical properties of bench marked upland soils in Korea, *Korean J. Soil Sci.* **34**, 326-332.
- Kaasalainen, M. and Yli-Halla. M., 2003, Use of sequential extraction to assess metal partitioning in soils, *Environ. Pollut.*, **126**, 225-233.
- Kim, T.H., 2010, Efficiency of chemical remediation technology and stabilization mechanism in heavy metal contaminated soil, Kangwon National University Graduate School Master's degree Collection of dissertations.
- Kim, J.Y., Davis, A.P., and Kim. K.W., 2003, Stabilization of available arsenic in highly contaminated mine tailings using iron, *Environ. & Technol.*, **37**(1), 189-195.

- Kim, J., Kim, K., and Lee, J., 2002, Assessment of arsenic and heavy metal contamination in the vicinity of Duckum Au-Ag mine, *Environ. Geochem. Hlth.*, **24**, 215-227.
- Ministry of Environment (MOE), 2010, Water Quality Conservation Act, Korea.
- Ministry of Environment (MOE), 2009a, Soil conservation Act, Korea.
- Ministry of Environment (MOE), 2009b, Standard Methods for Examination of Soil, Ministry of Environment notification, 186.
- Mireco., 2009, Research project for obtain basic data to mine pollution prevention project, Mireco, Seoul, Korea.
- Kumpiene, J., Lagerkvist, A., and Maurice, C., 2008, Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments - A review, *Waste Manage.*, **28**, 215-225.
- Lothenbach, B., Furrer, G., Scharli, H., and Schulin, R., 1999, Immobilization of zinc and cadmium by montmorillonite compounds: Effects of aging and subsequent acidification, *Environ. Sci. Technol.*, **32**, 2945-2952.
- Lee, J.W., 2007, Study on the management of abandoned metal mines after restoration, Kwangwoon University Graduate School Master's degree Collection of dissertations.
- Lee, M., Paik, I.S., Kim, I., Kang, H., and Lee, S., 2007, Remediation of heavy metal contaminated groundwater originated from abandoned mine using lime and calcium carbonate, *J. Hazard. Mater.*, **144**(1), 208-214.
- Ok, Y.S., Yang, J.E., Zhang, Y.S., Kim, S.J., and Chung, D.Y., 2007, Heavy metal adsorptions by a formulated zeolite-Portland cement mixture, *J. Hazard. Mater.*, **147**(1), 91-96.
- Park, D.H., Cho, Y.C., and Choi, S.I., 2010, The laboratory column examination of stabilization for agricultural land contaminated by heavy metals using sequential stabilization, *Soil Groundwater Env.*, **15**, 39-45.
- Ramsey, M.H., Thompson, M., and Banerjee, E. K., 1987, Realistic assessment of analytical data quality from induced coupled plasma atomic emission spectrometry, *Anal. Proc.*, **24**, 260-265.
- Shin, I.J., 2003, Translocation of heavy metals to some crops in paddy and upland soil around abandoned mines, Chungnam National University Graduate School Master's degree Collection of dissertations.
- Tessier, A., Campbell, P.G.C., and Bisson, M., 1979, Sequential extraction procedure for the speciation of particulate trace metals, *Anal. Chem.*, **51**, 844-851.
- Ullrich, S.M., Michael H.R., and Edeltrauda H.R., 1999, Total and exchangeable concentrations of heavy metals in soils near Bytom, an area of Pb/Zn mining and smelting in Upper Silesia, Poland, *Appl. Geochem.*, **14**(2) 187-196.
- Yang, J.E., Kim, J.S., Ok, Y.S., Kim, S.J., and Yoo, K.Y., 2006, Capacity of Cr(VI) reduction in an aqueous solution using different sources of zerovalent irons, *Korean J. Chem. Eng.*, **23**(6), 935-939.
- Yun, S.W., Kang, S.I., Jin, H.G., Kim, H.J., and Yu C., 2011, Leaching characteristics of arsenic and heavy metals and stabilization effects of limestone and steel refining slag in a reducing environment of flooded paddy soil, *J. agriculture & life science*, **45**(6), 251-263.