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Immobilization of heavy metals in a contaminated soil using organic sludge char and other binders

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Abstract−The applicability of tannery (TSC) and dye sludge char (DSC) as a binder to immobilize heavy metals (Zn, Cu and Ni) in soil was investigated. The toxicity characteristic leaching procedure (TCLP) was used to estimate the immobilization efficiency for single-binders (TSC and DSC) and binary-binders (TSC or DSC combined with tripostassium phosphate (K_3PO_4) diammonium phosphate (DAP), lime or ladle slag). The immobilization efficiencies of Zn, Cu and Ni by TSC amendment were 84.2, 100.0 and 40.0%, respectively, which were higher than 28.5, 100.0 and 54.9% by DSC amendment for a binder dose of 0.80 g char/g soil. The binary-binder enhanced Zn immobilization to 56.3 and 97.2% at 0.6 g-DSC/0.06 g-$Ca(OH)_2$ and 0.4 g-TSC/0.08 g-$Ca(OH)_2$, respectively per 1 g dried soil. The immobilization efficiencies of heavy metals increased with aging for the DSC-binary binders, but not for TSC-binary binders.

Key words: Char, Dye Sludge, Heavy Metals, Immobilization, Tannery Sludge

INTRODUCTION

A great deal of organic sludges disposed from dyeing industries and tannery processing industries can generate complex problems due to exposure of toxic Cr from tannery sludge and other heavy metals and organics from dye sludge to the natural environment. Various methods such as ocean disposal, incineration, drying and direct land filling have been used for the treatment of the organic sludges. But these methods have varying degree of environmental impact, and the potential risk to the human body through food-chain transfer still remains. The reuse of organic sludge such as tannery and dye sludge for soil amendment can alleviate disposal problems and give economic and ecological benefits.

Soils contaminated with metals and metalloids such as Zn, Cu, Ni, Cr(VI), As, Hg, Cd and Pb are of great concern because of their toxicities. The contamination is caused by the discharge of waste and wastewater from industrial and mining activities. Sustainable management of contaminated soils is important to protect the natural resources and to prevent human beings from direct and/or indirect exposure of heavy metals.

Sludge treatment at high temperature under oxygen-depleted conditions can reduce the sludge volume and leaching potential of heavy metals [1,2]. Biomass treated at high temperature under oxygen-depleted conditions produces char with high surface area [3]. Biochar is a kind of charcoal that has been produced under conditions to optimize its characteristics such as high surface area per unit volume [3,4]. The amendment of contaminated soil with woodchip-derived biochar can reduce the CO_2 production [5] as well as remove dissolved organic carbon (DOC) by adsorption [6]. Li et al. [7,8] reported that charred biomaterials such as charred woods, grass char, leaf char and charred woodchip adsorbed Cd(II), Cr(III) with high adsorption capacity and affinity.

Our previous study [9] showed that the BET surface area of tannery sludge increased from 1.695 to 6.875 m^2/g with the increase in the charring temperature from 350 to 550 °C, and subsequently the TCLP-extractable concentrations of heavy metals decreased. The charred sludge material is featured by high specific surface area and high mineral content (Ca and Al) due to charring at high temperature under oxygen-depleted conditions; thus it has a high potential as a binder to immobilize heavy metals. In addition, ash content increased with the increased charring temperature from 350 to 550 °C, but volatile matter (VM) and fixed carbon (FC) contents decreased.

Solidification/stabilization is an immobilization process of converting heavy metals with high mobility into solid form or physico-chemically stable form by chemical interactions among heavy metals, soil particles and binders. Various binders such as phosphate compounds, slag, lime and cement have been used for the immobilization of heavy metals. Lime, an alkaline material, is the most widely used for immobilization of heavy metals in soil. The lime reduces the mobility of heavy metals by an increase in pH, promoting the precipitation and formation of hydroxyl metal species [10]. The lime addition can enhance the pozzolanic reaction, resulting in the reaction of Ca supplied by lime with SiO_2 and Al_2O_3 present in soil to form C-S-H and C-A-H gels that are responsible for the development of binding strength [11,12]. Slag, an alkaline industrial by-product, has also received much attention because of low-cost and capability of immobilization. The presence of C-S-H compound [13], unhydrated C_3S ($3CaO \cdot SiO_2$), $Ca(OH)_2$, C-A-H ($CaO \cdot Al_2O_3 \cdot nH_2O$) and ettringite in slag induces the metal immobilization [14]. The heavy metals (Cr^{6+}, Cd^{2+}, Zn^{2+} and Pb^{2+}) were coated on their surfaces with the C-S-H gel and held them together, providing an effective shield against direct contact with leaching solution. The surface area coated with the gel (C-S-H gel) has high binding capacity per surface area. Therefore, a high degree of Cd^{2+} (>99.9%), Zn^{2+} (>99.9%), Pb^{2+} (99.9%), and Cr^{6+} (>98.8%) immo-

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bilization was observed [13]. The pozzolanic reaction to form C-S-H- gel and C-A-H gel is presented in detail by Eq. (1) and Eq. (2), respectively [15].

$$Ca(OH)_2+SiO_2+0.5H_2O \rightarrow CaO\cdot SiO_2\cdot 1.5H_2O \qquad (1)$$

$$4Ca(OH)_2+Al_2O_3+9H_2O \rightarrow 4CaO\cdot Al_2O_3\cdot 13H_2O \qquad (2)$$

Chen et al. [16] also reported that tricalcium silicate (C_3S, Ca_2SiO_4 CaO) is in contact with water, C-S-H gel is formed on the surface of C_3S grains and some heavy metal such as Cu^{2+}, Pb^{2+}, and Cr^{3+} accelerated the C_3S hydration and the formation of heavy metal double hydroxides ($Ca(OH)_2\cdot xM(OH)_2\cdot yH_2O$). However, in case of Zn^{2+}, C_3S hydration can arise from the precipitation of calcium zincate ($CaZn_2(OH)_6\cdot 2H_2O$) [16].

In-situ phosphate immobilization has been considered as an economically feasible and environmentally attractive method due to its effectiveness in reducing the leaching potential of heavy metals without excavation of the soil from the ground [17]. Amendment of heavy metal-contaminated soil by phosphate resulted in the conversion of highly available heavy metals to the most strongly bound or residual fraction [18]. Phosphates were highly effective for the immobilization of Pb through the formation of pyromorphite-like minerals [19-23]. However, the effectiveness of phosphate in the immobilization of Zn, Cd and Cu was less than that of Pb [19,22,24].

Lower et al. [25] reported that the hydroxyapatite (HAP) is dissociated into calcium and phosphate ions, and then the phosphate ion reacts with dissolved Pb to form hydroxyl-pyromorphite. These reactions are represented by Eq. (3) and Eq. (4), respectively.

$$Ca_5(PO_4)_3OH(s)+7H^+ \rightarrow 5Ca^{2+}+3H_2PO_4^-+H_2O \qquad (3)$$

$$5Pb^{2+}+3H_2PO_4^-+H_2O \rightarrow Pb_5(PO_4)_3\,(OH)(s)+7H^+ \qquad (4)$$

The objectives of this study were i) to evaluate the applicability of tannery (TSC) or dye sludge char (DSC) alone or in combination with other binders (K_3PO_4, DAP, lime or ladle slag) and ii) to evaluate the effect of aging in the immobilization of the heavy metals in the field-contaminated soil.

MATERIALS AND METHODS

1. Contaminated Soil

Heavy metal-contaminated soil was obtained from a former steel refinery site in Ulsan (Ulsan soil hereafter), Korea. The collected soil sample was dried at 60 °C for 48 h, ground, sieved through 600 μm mesh (sieve #30) and homogenized well by tumbling at 6 rpm in a tumbler for 24 hrs. The homogenized soil was kept in airtight plastic bottles prior to use. Background concentrations of heavy metals in the soil and charred sludge (DSC and TSC) were determined by microwave acid digestion using a microwave accelerated reaction system (MARS 5, CEM Corp., Matthews, NC, USA) based on USEPA SW846, method 3051 [26]. In brief, 10 mL of *aqua regia* solution (HNO_3 : HCl=1 : 3) was added in an Omni^{TM} vessel containing 0.5 g of the soil or organic sludge char or binder, and then digested in the microwave at 175 °C for 10 min and allowed to cool. After cooling, the digest was centrifuged for 20 min at 1,200 *g*, and the supernatant was filtered through the 0.20 μm syringe filter (Whatman, cellulose nitrate membrane filter, ϕ=25 mm), and then analyzed by inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer, 2100DV).

2. Binders

Tannery and dye sludges were obtained from a local tannery industry located in Busan, Korea and Korea Dyeing Technology Centre located in Daegu, Korea, respectively. The TSC and DSC were prepared by charring the tannery and dye sludges, respectively, at 550 °C under oxygen depleted conditions using a charring process at the Korea Dyeing Technology Center. Both TSC and DSC were ground and sieved through 212 μm mesh, and then mixed well for homogenization in a tumbler. The homogenized TSC and DSC samples were kept in airtight plastic containers before use. K_3PO_4 (Junsei Chemical Co., Ltd., Japan, >98.0%), DAP (diammonium phosphate, Fluka, >98.0), lime ($Ca(OH)_2$, >95%, Chungmoo Chemical Co., Korea), and ladle slag (POSCO, Pohang, Korea) were also ground and sieved through 212 μm before use.

3. Immobilization of Heavy Metals

Single-binder (TSC or DSC alone) and binary-binders (TSC or DSC+K_3PO_4, DAP, $Ca(OH)_2$ or ladle slag) were used for the immobilization of heavy metals in the contaminated soil. For single-binder experiment, 0.4, 0.6, 0.8 or 1.0 g of TSC or DSC was added into a 50-mL polycarbonate centrifuge tube (Nalgene Co., USA) containing 1 g of the contaminated soil. The mixture was thoroughly mixed using a vortex mixer (IKA® mini-shaker MS1) for 20 s, and then distilled and deionized (DI) water was added to adjust the water content to 50% (w/w). The mixture was allowed to stand for one day at room temperature. The binary-binder experiments were conducted in the same manner as in the single-binder experiments. The effect of aging (1, 7 and 30 d) on heavy metals immobilization was also investigated for the single- and binary-binders experiments. All experiments were conducted in duplicate.

4. Extraction Procedures

After immobilization, the leaching potential of heavy metals was evaluated by toxicity characteristic leaching procedure (TCLP, USEPA 1989, SW-846 Method 1311) [27]. Briefly, 20 mL of acetic acid solution prepared by dissolving 5.7 mL of glacial acetic acid (99%) in 1 L of DI water was added into the 50 mL polycarbonate centrifuge tube containing 1 g of immobilized soil (liquid : solid ratio= 20 : 1). The pH of the extraction solution was 2.88±0.05. The mixture was shaken for 24 h at 200 rpm on a horizontal orbital shaker (DR 302 DF, Daeryun Scientific Co., Korea). The samples were centrifuged for 20 min at 1,200 *g* and then the pH of the supernatant was measured. The supernatant was filtered through the syringe filter and then analyzed using the ICP-OES. Wavelength for Pb, Zn, Ni, Cu, Cd and Cr was 220.35, 206.20, 231.60, 327.39, 228.80 and 267.72, respectively. Limit of detection (LOD) was 0.02 mg/L for Pb, Ni, Cd, Cu and Cr and was 0.04 mg/L for Zn.

5. Microstructure Analysis

Microstructure analyses were conducted to determine surface characteristics, morphology of the soil samples before and after immobilization. The surface characteristics of the soil samples were investigated using an SEM (Scanning Electron Microscopy, S-4300, Hitachi, Japan) to analyze the changes in shape, size and morphology before and after immobilization. Mineral compositions of the binders were also investigated using X-ray fluorescence (XRF, PW2400, Philips Electronic Instruments, Inc., The Netherlands) and identified by X-ray diffraction (XRD, D/Max-2500, Rigaku, The Netherlands). The EDS (Energy Dispersive X-ray Spectroscopy, S-4800,

Table 1. Total and TCLP-extractable heavy metal concentrations in the soil, TSC and DSC

Heavy metals	Concentration (mg/kg dry weight)				TCLP regulatory level (mg/L)
	Soil		TSC	DSC	
	Total	TCLP (mg/L)			
Pb	17	0	107	208	5
Cr	88	0.013	31,776	357	5
Zn	6,945	59.0	1,608	869	-
Cu	90	0.290	1,089	448	-
Ni	43	0.229	307	243	-

Hitachi, Japan) analyses were conducted to identify the chemical compositions of the samples.

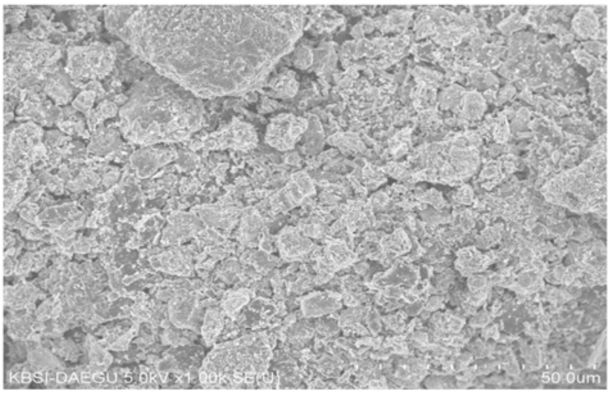
RESULTS AND DISCUSSION

1. Physicochemical Characteristics of Soil and Binders

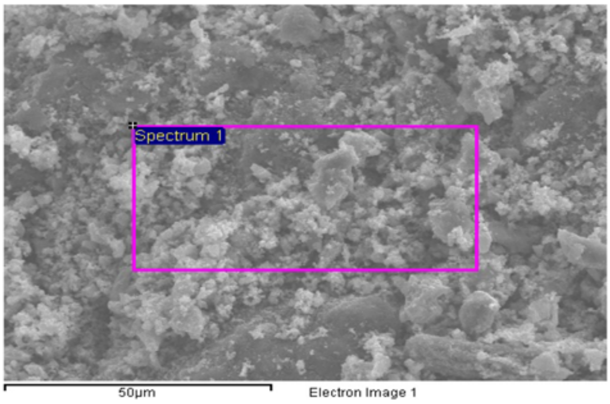
The physicochemical characteristics of the contaminated soil and the binders were analyzed. The pH of the soil is about 6.6 and the water content is 21.4%. Point of zero charge measured by Appel et al. [28] was about 4.5. The organic carbon content is 0.264. Background concentrations of heavy metals in the contaminated soil determined by microwave assisted acid digestion [26] are presented in Table 1. Zn (6,945 mg/kg) was the most abundant heavy metal in the soil followed by Cu (90 mg/kg), Cr (88 mg/kg), Ni (42 mg/kg) and Pb (17 mg/kg). As expected, TSC contained higher concentration of Cr (31,776 mg/kg) than DSC (357 mg/kg). Zn concentrations in TSC and DSC were 1,608 and 869 mg/kg, respectively. In the soil, TCLP-extractable Zn was 59.0 mg/L. Other TCLP-extractable heavy metals (Pb, Ni, Cu and Cr) were less than 10 mg/kg. Particularly, Cr(VI) concentrations were under the USEPA limit (5 mg/L for TCLP criteria) even after TSC and DSC were amended into the soil by 1 : 1 wt ratio (data not shown). The TSC did not contain TCLP-extractable Zn and Cu, but DSC contained 1.33 mg/L of Zn and 0.064 mg/L of Cu.

SEM photographs of the untreated soil (control), TSC and DSC are shown in Fig. 1. The soil sample had bigger crystal size and more porous surface than the DSC and TSC. EDS analysis indicated that the soil contained Al and Si; and DSC and TSC contained Ca and Fe. Ca intensity in TSC was higher than that in DSC (Fig. 2). The Ca content in the binder or soil is important in the pozzolanic reaction with SiO_2 and Al_2O_3. XRD analysis indicated that SiO_2 is a dominant mineral in the soil (Fig. 3). Calcite ($CaCO_3$) peaks were observed in TSC at different 2θ values. Singh and Pant [29] reported that calcite crystal present in the immobilized soil filled the pores in the soil mixture and enhanced the immobilization of heavy metals in the contaminated soil. In DSC, no calcite but magnetite (Fe_2O_3) peaks were observed.

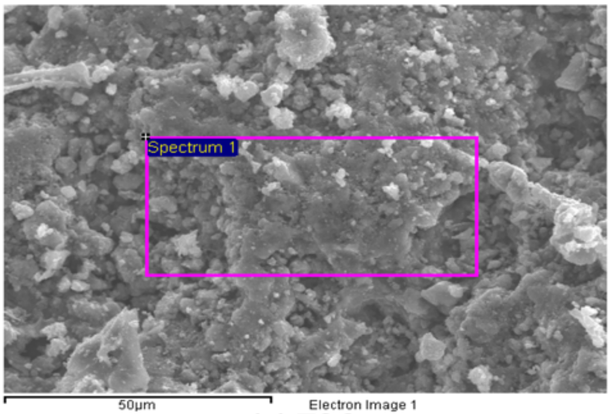
Chemical compositions of the soil and the binders determined by XRF analyses are listed in Table 2. In the contaminated soil, the CaO content (0.25%) was much lower than SiO_2 (18.46%), Al_2O_3 (11.55%) and Fe_2O_3 (18.59%) contents. The CaO content in the binders was in the order of lime (97.1%)>ladle slag (57.86%)>TSC (10.4%)>DAP (2.86%)>DSC (2.4%). SiO_2 (11.1%) and Al_2O_3 (22.5%) were the major minerals in the ladle slag. Therefore, the main mechanisms for the immobilization of heavy metals were C-S-H and C-A-H formation of the pozzolanic reaction because all binders had high CaO content except DAP and DSC. The P_2O_5 content (75%) in DAP indicates that pyromorphite formation would be the main mechanism of heavy metals immobilization.



(a) Soil



(b) DSC



(c) TSC

Fig. 1. SEM photographs of (a) Soil, (b) dye sludge char (DSC) and (c) tannery sludge char (TSC).

2. Immobilization of Heavy Metals by Single-binders

After immobilization of heavy metals by single-binder such as TSC or DSC for 1-d, the immobilization efficiency was evaluated by TCLP (Fig. 4). The TCLP-extractable Zn concentration in the soil was 59.0 mg/L, but those of other heavy metals (Pb, Ni, Cu, and Cr) were very low. Thus, only Zn was analyzed hereafter. The TCLP-

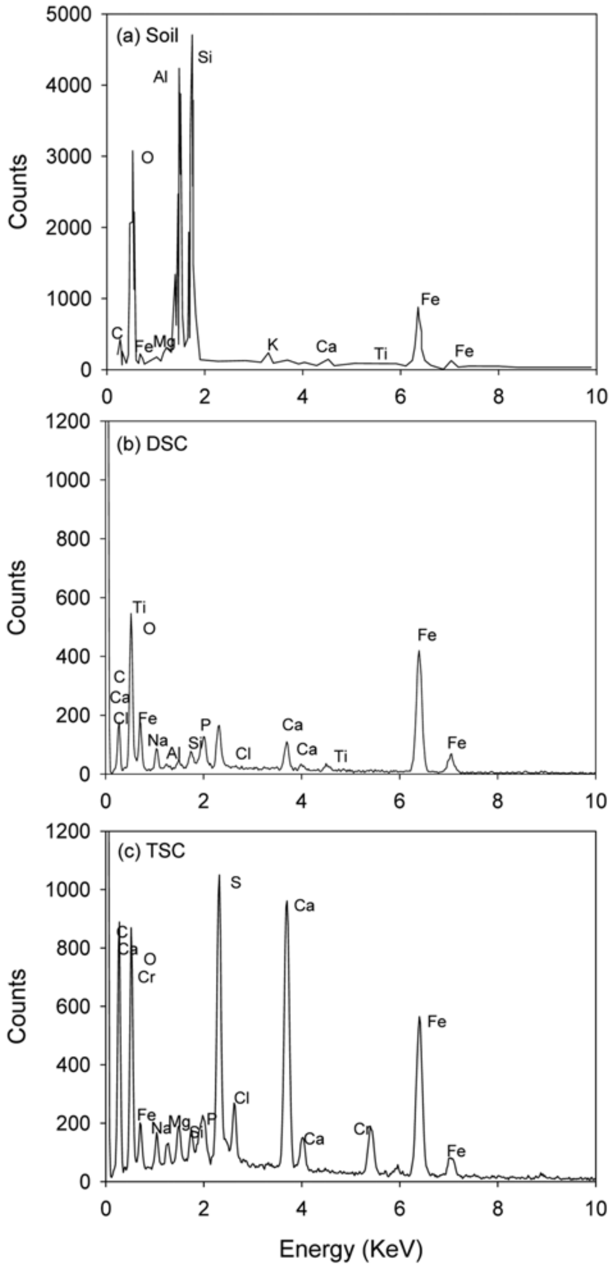


Fig. 2. EDS peaks of (a) Soil, (b) DSC and (c) TSC.

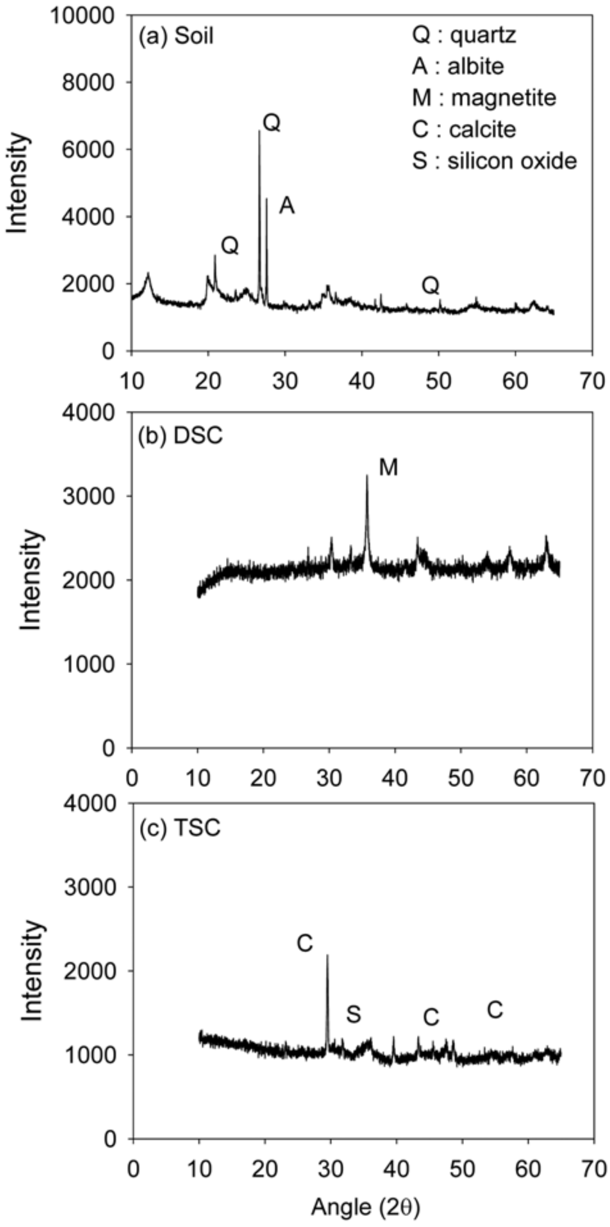


Fig. 3. XRD analyses of (a) Soil, (b) DSC and (c) TSC.

extractable Zn concentration decreased from 59.0 to 6.17 mg/L or 40.2 mg/L after the amendment of 1 g of TSC or DSC per 1 g of the soil, respectively. The immobilization efficiencies for heavy metals at the TSC dosage of 0.4, 0.6, 0.8 and 1.0 g/g soil were 50.6%, 70.0%, 84.1%, and 89.5%, respectively. The efficiency increased as TSC dosage increased, but increased more slowly at the TSC dosage above 0.8 g/g soil. The immobilization efficiency of Zn at DSC dosage of 0.4, 0.6, 0.8 and 1.0 g per g soil was only 10%, 22%, 28% and 31%, respectively. The Zn immobilization efficiency increased with DSC dosage but did not further increase at the DSC dosage above 0.6 g/g soil. The TCLP-extractable Ni concentration after the amendment of 0.8 g TSC or DSC per g soil decreased from 0.229 to 0.136 or 0.103 mg/L, respectively. The immobilization efficiency of Ni in the TSC-amended soil (40.0%) was lower than the DSC-amended soil (54.9%). Cu and Cr were not detected after the immobilization by TSC or DSC. Beesley and Marmiroli [30] observed that the Zn concentration in the pore water decreased after amendment of contaminated soil with wood-derived biochar; however, immobilization mechanisms involved were not explained. In our study, the Zn immobilization efficiency increased with TSC or DSC dosage due to the increased pozzolanic reaction caused by the higher CaO content in the TSC and DSC with SiO_2 and Al_2O_3 in the soil. In addition, the higher CaO content raised the pH to ~10 during immobilization with TSC and DSC, which led Zn to be precipitated in the form of $Zn(OH)_2$ [15]. The Ca content in TSC was higher than that in DSC, resulting in the formation of more C-S-H products available to bind the heavy metals in the TSC amended soil. The high Ca content in the TSC was confirmed by the EDS peaks in Fig. 2. XRD analyses also showed that calcite intensity in

Table 2. XRF analyses of soil sample and binders

	Chemical composition (%)					
Chemical compound	Soil	TSC	DSC	Ladle slag	Lime	DAP
MgO	0.53	-	-	2.82	0.88	1.51
Al_2O_3	11.55	0.86	0.39	22.50	0.28	1.99
SiO_2	18.46	1.12	1.82	11.10	0.82	1.49
P_2O_5	0.23	0.79	1.67	0.05	-	75.09
SO_3	-	7.42	2.86	0.82	0.14	12.31
Cl	-	1.64	ND	-	-	-
K_2O	1.16	0.18	0.23	0.15	0.08	0.86
CaO	0.25	10.42	2.42	57.87	97.15	2.87
TiO_2	1.09	0.22	1.98	0.24	-	-
Cr_2O_3	-	10.81	ND	-	-	-
MnO	0.30		ND	1.42		0.25
Fe_2O_3	-	64.54	86.82	2.95	0.52	3.54
CuO	-	0.55	ND	-	-	-
ZnO	0.45	0.71	0.23	-	-	0.07
Br	-	0.18	0.12	-	-	-
SnO_2	-	ND	1.06	-	-	-
SrO	-	ND	ND	0.07	0.12	
Sb_2O_3	-	ND	0.39	-	-	-
NiO	-	0.56	-	-	-	-
FeO_3	18.59	-	-	-	-	-

ND: not detected

TSC was higher than that in DSC (Fig. 3). Singh and Pant [29] explained that the presence of calcite in the amended soil filled up the pores in the soil, resulting in the reduced leaching potential of heavy metals from the soil. As TSC or DSC dosage increased, however, the Zn immobilization efficiency was not improved further, indicating that the use of TSC or DSC as a single-binder for the immobilization of heavy metals is rather limited. The optimum dosage of TSC and DSC was 0.8 g and 0.6 g per 1 g soil, respectively.

3. Immobilization of Heavy Metals by Binary-binders

To improve the immobilization efficiencies of heavy metals by the single-binder (i.e., DSC or TSC alone), the binary-binders consisting of DSC or TSC and K_3PO_4, DAP, $Ca(OH)_2$ or ladle slag were applied. Amendments by binary-binders consisting of 0.6 g of DSC +K_3PO_4, DAP, $Ca(OH)_2$ or ladle slag were applied for the immobilization of heavy metals in 1.0 g of contaminated soil and the immobilization efficiency was evaluated by TCLP (Fig. 5). There were no significant changes in immobilization efficiency of heavy metals including Cu and Ni by the amendment of binary binders compared to single binders except for Zn, thus only Zn was discussed hereafter. The TCLP-extractable Zn concentrations decreased as the other binder (K_3PO_4/DAP/lime/ladle slag) dosage increased from 0.02 g/g dry soil to 0.06 g/g dry soil. The immobilization efficiency of Zn at the 0.60 g of DSC+0.06 g of K_3PO_4/DAP/$Ca(OH)_2$//ladle slag was in the order of DSC+ladle slag (70.9%, 17.1 mg/L)>DSC+$Ca(OH)_2$ (59.0%, 24.2 mg/L)>DSC+DAP (58.4%, 24.6 mg/L)>DSC +K_3PO_4 (56.3%, 25.8 mg/L). Therefore, the binary-binders composed of DSC and other binders were not suitable for Zn immobilization in the soil (<70%).

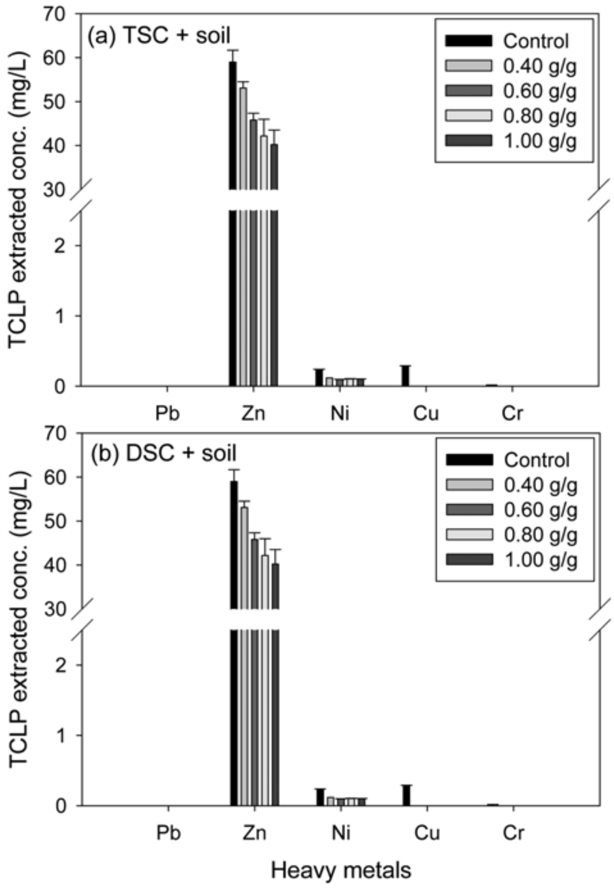


Fig. 4. TCLP-extractable heavy metal concentrations in the soil after 1-d immobilization by single-binders.

Immobilization efficiency of Zn at the binder dosage of 0.4 g TSC+ (0.02 to 0.08 g) K_3PO_4/DAP/$Ca(OH)_2$/ladle slag per 1 g of soil was evaluated by TCLP (Fig. 6). The immobilization efficiencies increased as the binder dosage increased. Immobilization efficiency of Zn at the binary-binder dosage of 0.4 g TSC+0.06 g K_3PO_4/DAP/$Ca(OH)_2$/ ladle slag per g soil was in the order of TSC+ladle slag (79.1%, 12.3 mg/L)>TSC+$Ca(OH)_2$ (71.2%, 17.0 mg/L)>TSC+DAP (70.2%, 17.6 mg/L)>TSC+K_3PO_4 (65.3%, 20.6 mg/L).

In Fig. 6, TSC+$Ca(OH)_2$ and TSC+ladle slag were more effective than TSC+K_3PO_4 and TSC+DAP in Zn immobilization. Clearly, the Zn immobilization efficiencies of all TSC-binary-binders were higher than that in DSC-binary-binders even though TSC dosage (0.4 g/g dry soil) was less than DSC (0.6 g/g dry soil) dosage. This is attributed to the higher CaO content in TSC (10.4%) than in DSC (2.4%) (Table 3). The higher CaO content in TSC, lime, and ladle slag facilitates the pozzolanic reaction with SiO_2 and Al_2O_3 present in the soil to form C-S-H and C-A-H, thereby reducing the mobility of heavy metals. The immobilization efficiency of Zn at the 0.4 g TSC+0.08 g $Ca(OH)_2$/ladle slag was 97.2% and 92.9%, respectively, showing the highest immobilization efficiency by the binary-binder 0.4 g TSC+0.08 g $Ca(OH)_2$ per g soil.

Phosphate binders (DAP and K_3PO_4) were poor in the Zn immobilization. The Zn immobilization by phosphate amendment was attributed to pyromorphite formation as reported by Lower et al. [25]. The phosphate in the DAP and K_3PO_4 reacts with heavy metal

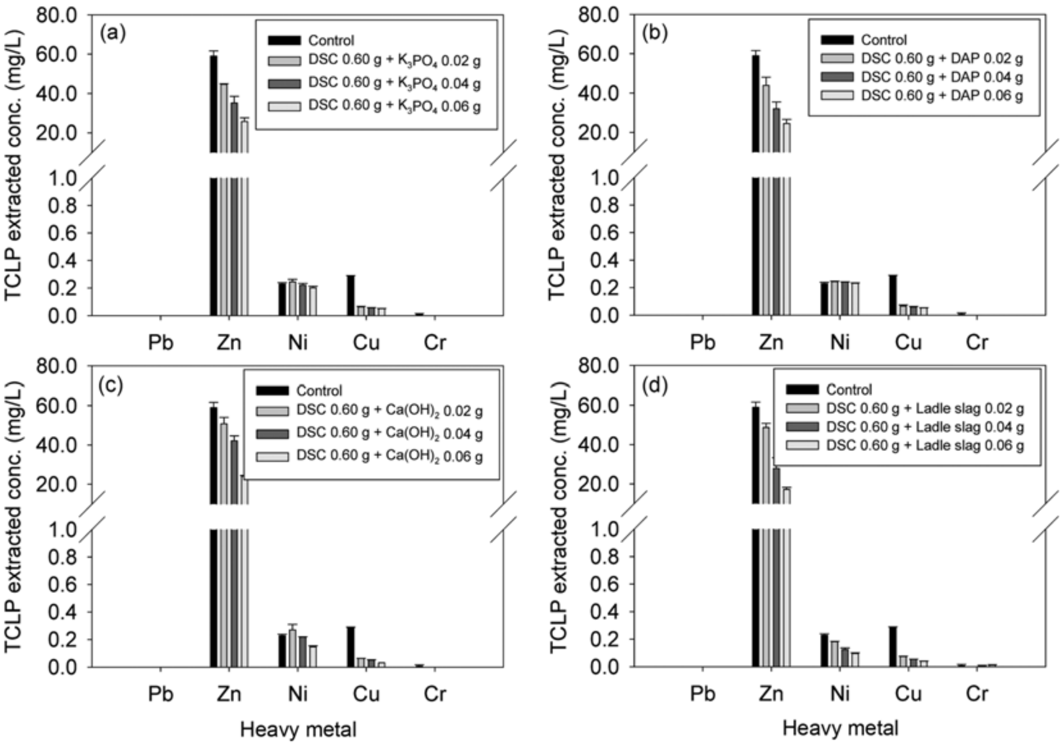


Fig. 5. TCLP-extractable heavy metal concentrations in the soil after 1-d immobilization by binary-binders, DSC+(a) K_3PO_4, (b) DAP, (c) $Ca(OH)_2$ and (d) ladle slag per g soil.

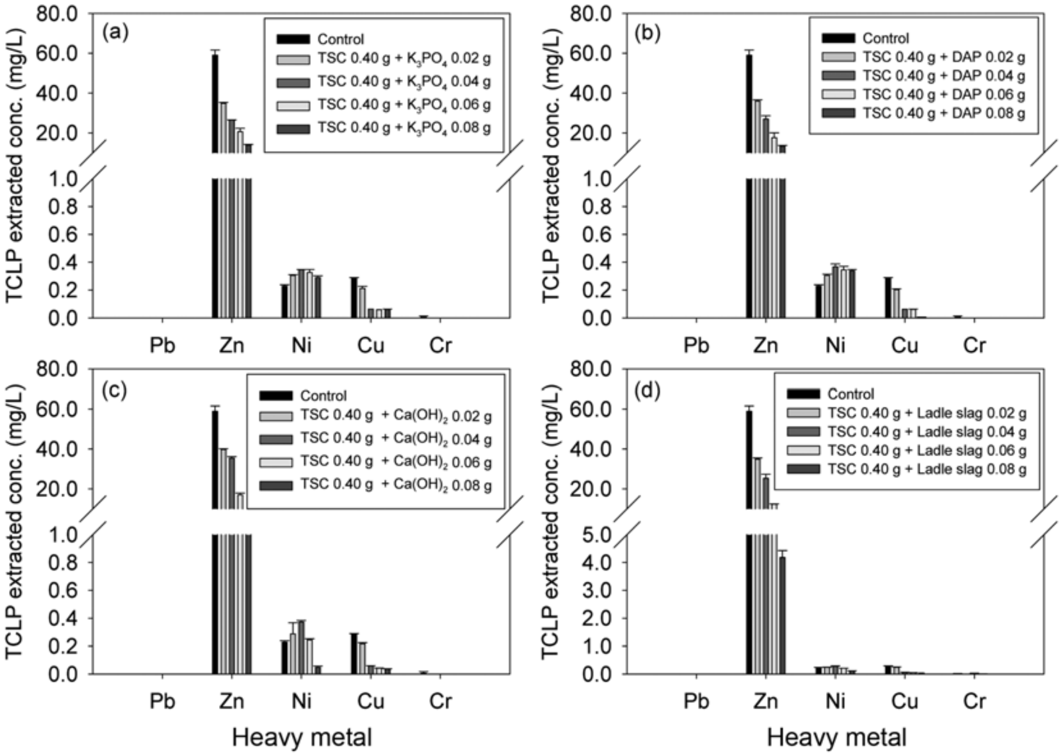


Fig. 6. TCLP-extractable heavy metal concentrations in the soil after 1-d day immobilization by binary-binders, TSC+(a) K_3PO_4, (b) DAP, (c) $Ca(OH)_2$ and (d) ladle slag per g soil.

to form a stable mineral, pyromorphite. However, in our study, the pyromorphite formation by phosphate amendments was not sufficient to immobilize Zn in the soil. As shown by XRF analyses, the increase of P_2O_5 content was low in the DSC+K_3PO_4/DAP amended

Table 3. XRF analyses of the soil before and after immobilization

Chemical compound	Soil	Chemical composition (%)							
		Soil immobilized by DSC+other binders				Soil immobilized by TSC+other binders			
		Ladle slag	$Ca(OH)_2$	K_3PO_4	DAP	Ladle slag	$Ca(OH)_2$	K_3PO_4	DAP
MgO	0.53	-	-	-	-	-	-	-	-
Al_2O_3	11.55	13.01	11.22	10.50	11.40	15.20	12.48	12.30	13.29
SiO_2	18.46	21.48	19.52	18.45	20.41	23.80	21.96	21.19	23.58
P_2O_5	0.23	0.201	0.16	0.29	0.51	0.12		0.32	0.57
SO_3	-	0.32	0.33	0.24	0.32	0.35	0.35	0.38	0.34
K_2O	1.16	1.57	1.54	4.88	1.62	1.69	1.72	7.32	1.99
CaO	0.25	4.04	6.72	1.10	1.11	7.88	11.75	3.14	3.37
TiO_2	1.09	2.25	2.26	2.35	2.30		1.94	1.89	1.99
Cr_2O_3	-	-	-	-	-	2.89	2.57	2.81	2.72
MnO	0.30	0.59	0.56	0.59	0.54	0.72	0.64	0.64	0.71
Fe_2O_3	-	55.65	56.65	60.55	60.81	44.44	45.46	48.80	50.09
ZnO	0.45	0.87	1.02	1.06	1.0	1.04	1.142	1.22	1.35
FeO_3	18.59	-	-	-	-	-	-	-	-

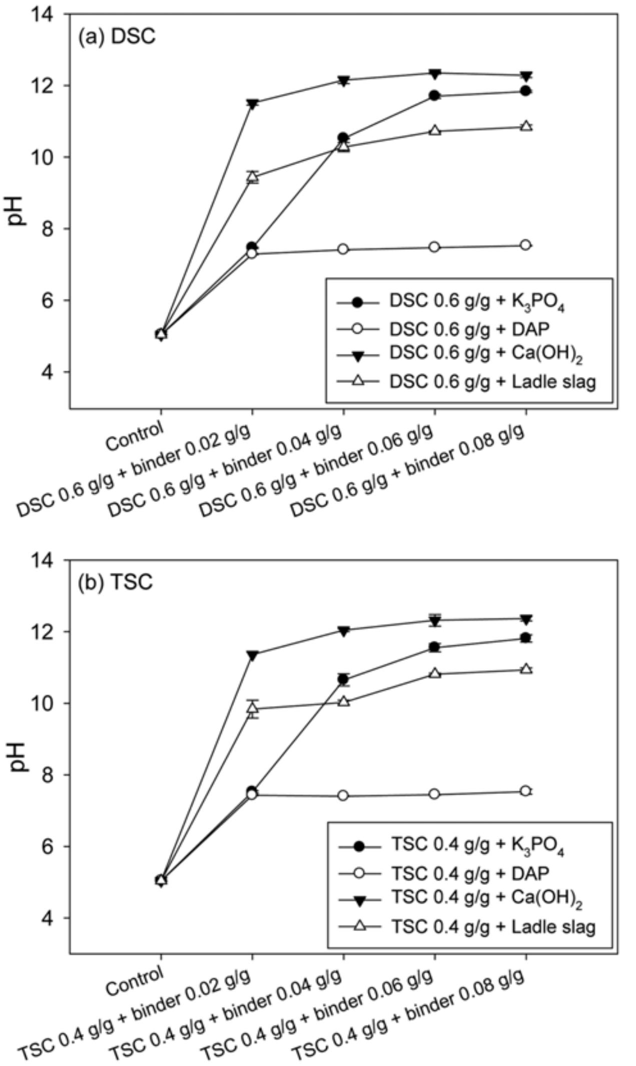


Fig. 7. pH of soil after 1-d immobilization by binary-binders. (a) DSC and (b) TSC.

soil (Table 3). Other researchers also reported that phosphate binders were efficient for Pb but not for Zn [19,24]. Solubility product (K_{sp}) of lead hydroxypyromorphite ($Pb_5(PO_4)_3OH$, $=5.01\times10^{-83}$) was much less than that of zinc hydroxy-pyromorphite ($Zn_5(PO_4)_3OH$, $=7.94\times10^{-64}$). The stability of $Zn_5(PO_4)_3OH$ was lower than that of $Pb_5(PO_4)_3OH$, resulting in the less immobilization of Zn by the phosphate amendment [31]. As shown in Fig. 7, the soil pH after binary-binder amendment increased with binder dosage. The pH was in the order of DSC or TSC+$Ca(OH)_2$>+K_3PO_4>+Ladle slag>+DAP. Phair and Van Deventer [32] explained that at higher pH (>12) higher cationic heavy metals (Pb and Cu) are likely to react with silica or hydroxide present in the fly ash, reducing the solubility of the heavy metals. They further explained that the leachability of heavy metals not only depends on the solubility of the metal precipitate but also on the permeability of the solute.

4. Effect of Aging on the Immobilization by Binary-binders

Effect of aging (1-d, 7-d, and 30-d) on the immobilization of heavy metals by binary-binders was evaluated by TCLP (Fig. 8). The TCLP-extractable Zn concentration decreased as aging increased from 1-d to 30-d. The TCLP-extractable Zn concentrations from 0.6 g DSC+ 0.08 g K_3PO_4/0.08 g DAP/0.04 g $Ca(OH)_2$/0.06 g ladle slag amended soils after 1-d aging were 25.8, 24.6, 42.2 and 17.1 mg/L, respectively. The Zn concentrations were further reduced to 19.0, 17.8, 40.0 and 17.2 mg/L, respectively, after 7-d aging. In the phosphate (DAP and K_3PO_4) amendments, Zn immobilization efficiency after 7-d aging increased due to stable phosphate mineral formation, but the increase in the immobilization efficiency was reduced after 30 days. In case of lime and ladle slag, the increase in the immobilization efficiency after 30 days was higher than after 7 days. It could be due to continuous utilization of SiO_2 and Al_2O_3 in the soil and CaO in the binders (ladle slag and lime) by pozzolanic reaction.

The TCLP-extractable Zn concentrations in 0.4 g TSC+0.08 g K_3PO_4/0.08 g DAP/0.04 g $Ca(OH)_2$/0.06 g ladle slag amended soils were 13.9, 13.3, 35.4 and 12.3 mg/L, respectively, after 1-d aging. The concentrations were 16.0, 12.3, 34.4 and 12.7 mg/L, respectively, after 7 d aging (See Fig. 9). Unlike in DSC-binary-binder

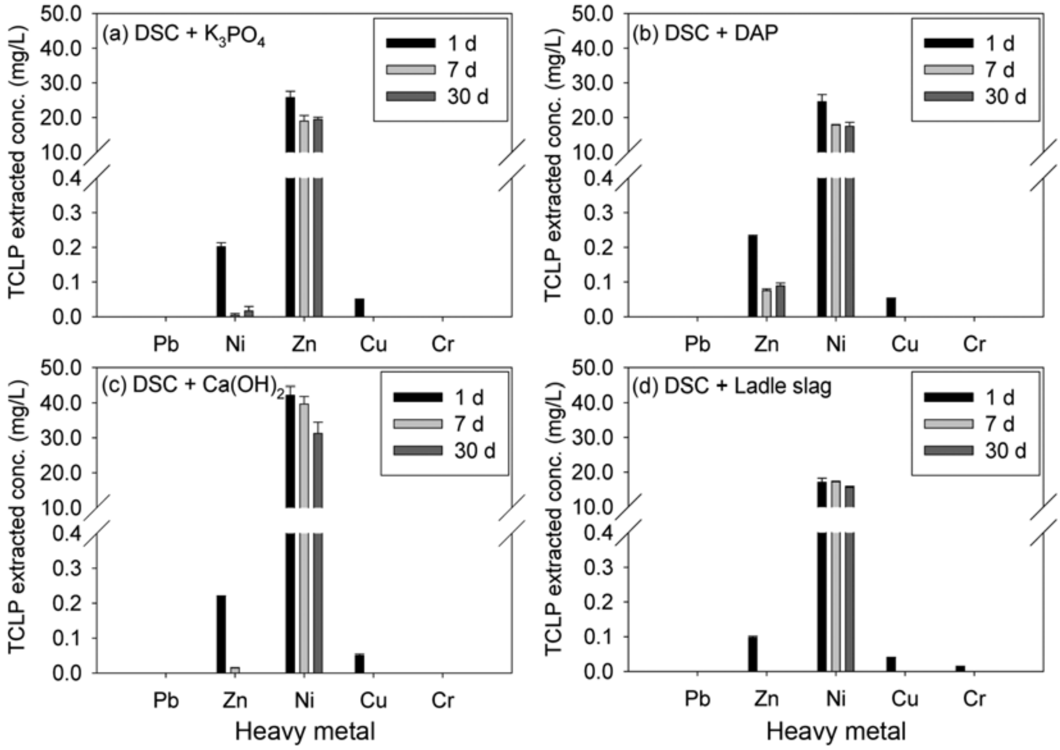


Fig. 8. Effect of aging on the immobilization of heavy metals by binary-binders, 0.6 g DSC+(a) 0.08 g K_3PO_4, (b) 0.08 g DAP, (c) 0.04 g $Ca(OH)_2$ and (d) 0.06 g ladle slag per g soil.

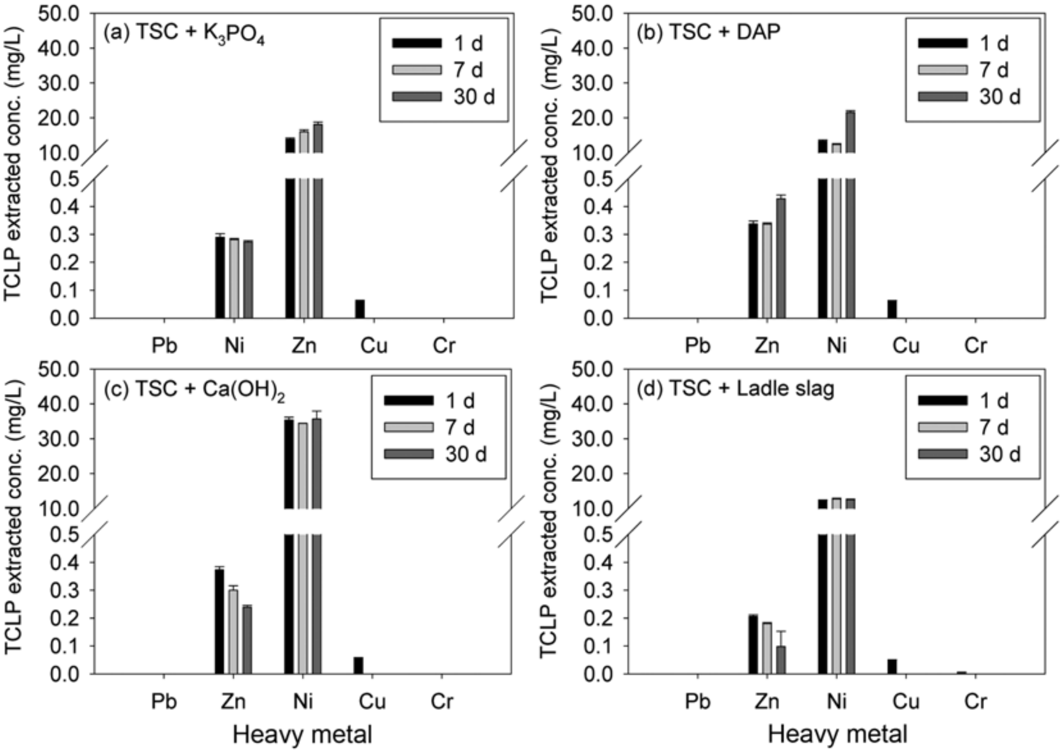
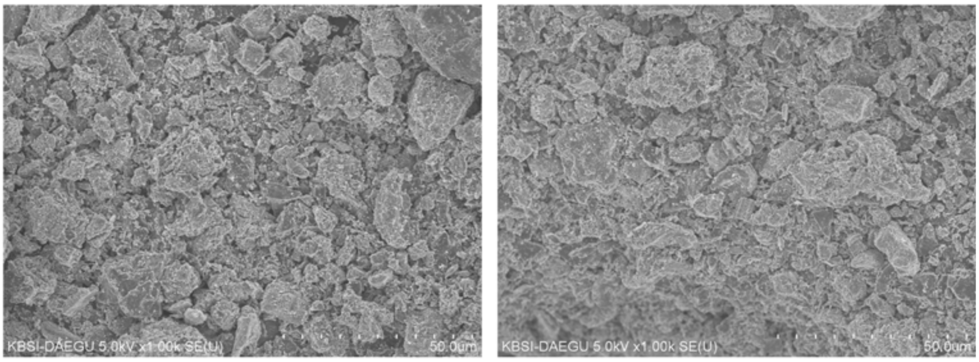
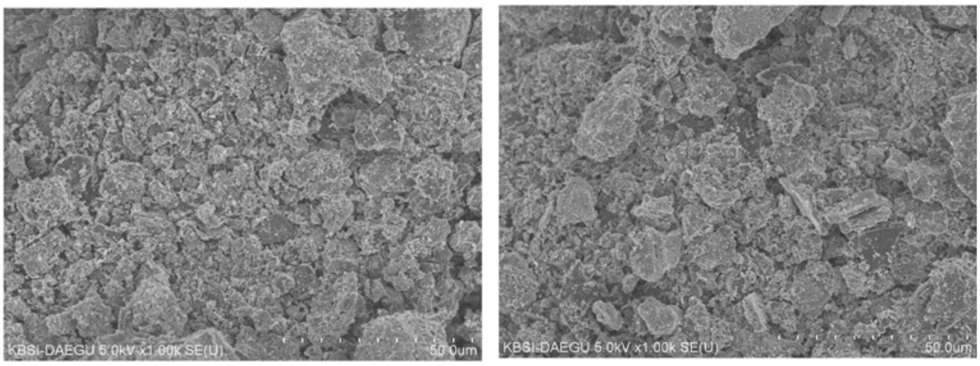


Fig. 9. Effect of aging on the immobilization of heavy metals by binary-binders, 0.4 g TSC+(a) 0.08 g K_3PO_4, (b) 0.08 g DAP, (c) 0.04 g $Ca(OH)_2$ and (d) 0.06 g ladle slag per g soil.

amended soil, there was not much deviation in the increase or decrease of Zn after 7 days. After 30-d aging, the TCLP-extractable Zn concentration slightly increased in the 0.4 g TSC+0.04 g lime (0.71%) and the 0.4 g TSC+0.06 g ladle slag (1.91%) amended soils,

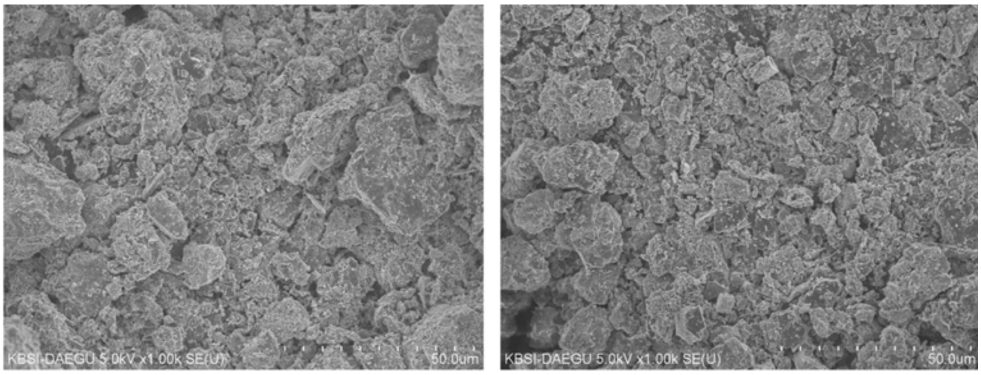


(a) DSC + K_3PO_4 + Soil (b) DSC + DAP + Soil

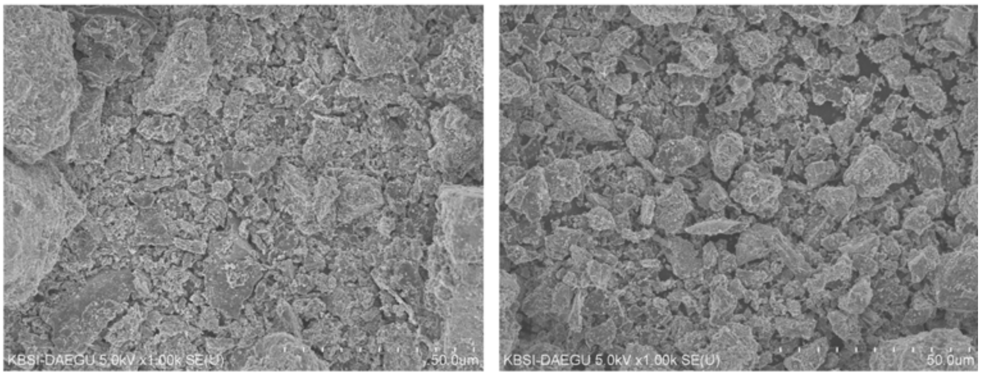


(c) DSC + lime + Soil (d) DSC + ladle slag + Soil

Fig. 10. SEM photographs of the soil after 1-d immobilization by binary-binders, 0.6 g DSC+(a) 0.08 g K_3PO_4, (b) 0.08 g DAP, (c) 0.04 g lime and (d) 0.06 g ladle slag per g soil.



(a) TSC + K_3PO_4 + Soil (b) TSC + DAP + Soil



(c) TSC + lime + Soil (d) TSC + ladle slag + Soil

Fig. 11. SEM photographs of the soil after 1-d immobilization by binary-binders, 0.4 g TSC+0.08 g K_3PO_4, (b) 0.08 g DAP, (c) 0.04 g lime and (d) 0.06 g ladle slag per g soil.

Table 4. EDS peaks of P and Ca in 1d and 7d immobilized soil

Binders	P peaks			Ca peaks		
	KeV	1-d Counts	7-d Counts	KeV	1-d Counts	7-d Counts
DSC+K_3PO_4	1.88	396	685	3.58	-	342
DSC+DAP	1.89	580	1,134	3.56	232	513
DSC+lime	1.87	-	142	3.56	664	426
DSC+ladle slag	1.89	228	312	3.60	592	607
TSC+K_3PO_4	1.89	322	202	3.58	253	216
TSC+DAP	1.87	381	468	3.60	233	381
TSC+lime	-	-	-	3.60	1,719	1,233
TSC+ladle slag	-	-	-	3.60	662	592

but the increases were higher in the 0.4 g TSC+0.08 g K_3PO_4 (30.5%) and 0.4 g TSC+0.08 g DAP (61.7%) amended soils (Figs. 8 and 9). Increase of TCLP-extractable Zn after 30 days of immobilization in 0.4 g TSC+0.08 g K_3PO_4/0.08 g DAP amended soil indicates the reverse effect of these binders on specific heavy metal immobilization like Zn. Thus, among the binary binders, TSC+K_3PO_4/DAP was not suitable for the immobilization of heavy metals in the soil.

5. Microstructure Analysis of the Immobilized Soils

Changes in the morphology of the soil surface after amendments of the various binders were investigated by SEM photographs (Figs. 10 and 11). The TSC or DSC+lime/ladle slag amended soil had more compacted surface than TSC or DSC+DAP/K_3PO_4 amended soil. Generally, the amended soil with more compacted surface had higher immobilization efficiencies (See Fig. 5 and Fig. 10 for DSC; Fig. 6 and Fig. 11 for TSC). However, no other apparent change in the morphology of soil surface was found after immobilization.

EDS analyses confirmed that the immobilization efficiency of Zn in TSC+K_3PO_4/DAP/$Ca(OH)_2$/ladle slag amended soil was higher than that in DSC+K_3PO_4/DAP/$Ca(OH)_2$/ladle slag amended soil after 1-d immobilization (Table 4). Ca counts in TSC+lime/ladle slag amended soils were higher than those in DSC+lime/ladle slag amended soils. This indicates the higher pozzolanic reaction in TSC-binary-binder amended soil than that in DSC-binary-binder amended soil resulted in the higher Zn immobilization. However, although P count shows a higher value in DSC+K_3PO_4/DAP than in TSC+K_3PO_4/DAP, the immobilization efficiency in DSC+K_3PO_4/DAP was not better than that in TSC+K_3PO_4/DAP.

Effect of aging time (1-d and 7-d) on P and Ca counts in the immobilized soil with DSC-binary binders showed that those counts increased at 7-d aging time except for Ca counts in DSC-lime. The increase in P and Ca counts could explain the increase in Zn immobilization efficiency with aging time in DSC-binary binder. The P and Cd counts did not increase as the aging time increase from 1 to 7 days in TSC-binary binders, which were also consistent with the non-increase of the Zn immobilization efficient with aging time.

CONCLUSIONS

The immobilization of heavy metals using organic sludge chars, by-products from charring process was conducted. Immobilization of heavy metals (Pb, Ni, Zn, Cu, and Cr) in the field-contaminated soil was conducted by using single-binder (TSC or DSC alone) and binary-binders (TSC or DSC in combination with other binders; K_3PO_4, DAP, lime or ladle slag). The immobilization efficiencies of the heavy metals in the contaminated soil by the binder amendments were evaluated by TCLP. In single-binder amendments, TSC performed better than DSC in Zn and Cu immobilizations mainly due to the higher CaO, SiO_2 and Al_2O_3 contents in TSC, whereas DSC was better than TSC in Ni immobilization. However, the TSC or DSC as a single-binder was still not efficient in the immobilization of heavy metals in the soil, mainly due to insufficient Ca content in these binders. By combining TSC or DSC with ladle slag or lime (Ca source), immobilization efficiency was improved. Aging up to 30 days decreased Zn leaching from DSC+other binders amended soils, but not from TSC+other binders. Among the binary-binders, 0.4 g TSC+0.08 g $Ca(OH)_2$ per g soil was the best in the immobilization of Zn (97.2%) in the soil.

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