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Solidification/stabilization of heavy metals in tannery sludge char with various binders

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ABSTRACT

The leaching potential of heavy metals (Cr, Pb, Ni, Zn, and Cu) from the tannery sludge charred at above 350˚C under oxygen-depleted conditions was evaluated for re-use as landfill cover materials. Solidification/stabilization (S/S) was employed for the immobilization of heavy metals in the tannery sludge chars (TSCs) to further reduce the leaching potential. The effects of charring temperatures, different types of binders ($FeSO_4$, lime, cement, HAP, and ladle slag), and aging on the immobilization of heavy metals (Pb, Ni, Zn, Cu, and Cr) in the TSCs were investigated. The immobilization efficiencies were estimated using the toxicity characterization leaching procedure (TCLP). The results show that the extractable concentrations of heavy metals decreased with the charring temperature. The single binder ($FeSO_4$ alone) was highly effective for Cr immobilization, but not for other heavy metals such as Ni and Zn. The binary binders, $FeSO_4$ combined with lime, cement, or ladle slag, were highly effective in the simultaneous immobilization of Cr, Ni, and Zn. Among the binary binders, the $FeSO_4$ + lime was the best combination in the heavy metal immobilization. TCLP-extractable concentrations decreased after aging for 30 days. The metal immobilization efficiency increased with CaO and SiO_2 contents in the binders (lime > cement > ladle slag) and with aging.

Keywords: Binders; Char; Heavy metals; Immobilization; Solidification/stabilization; Tannery sludge

1. Introduction

Large amount of heavy metals including chromium and other chemicals such as proteins, polyphenolic compounds, surfactants, and dyes have been used in tanning process in which raw animal skins/hides are treated with a series of chemicals and transformed into leathers. The remaining dissolved chromium and other chemicals subsequently discharged into the wastewater after tanning process are removed through physicochemical treatment in the tannery wastewater treatment plants. Thus, the tannery sludge produced from the wastewater treatment plants contains remarkable concentrations of heavy metals, and other chemicals which require adequate

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treatment techniques to reduce the concentrations of them below the regulatory criteria [1]. Until now, various methods such as ocean disposal, incineration, drying and direct land filling have been used. However, such methods cannot completely prevent leaching of heavy metals into the nature.

Charring the sludge at high temperature under oxygen depleted condition can produce the sludge char or ash with high surface area which can effectively reduce the release of heavy metals [2,3] and also can reduce Cr^{6+} to less toxic Cr^{3+} present in tannery sludge [4]. Although this charring process has a promising potential to treat the sludges, leaching potential of heavy metals from the thermal-treated tannery sludge is still of concern, especially Cr leaching since the tannery sludge generally contains high Cr concentration. For this reason, an additional process to reduce the remaining leaching potential of heavy metals from the tannery sludge char (TSC) is required. Solidification/stabilization (S/S) has been considered as a solution to effectively reduce the mobility of heavy metals released from soils, sludges, etc.

Solidification/stabilization (S/S) is an immobilization process converting heavy metals with high mobility into solid form or physically and chemically stable form by chemical interactions between heavy metals and binders. Ca-containing binders, such as cement [5], lime [6–8] and slag [9,10], have been generally used for immobilization of heavy metals via pozzolanic reaction and thereby reducing the leaching potential because of its relatively low-cost, simplicity, as well as good efficiency [11]. The calcium contained in the cement, slag and lime reacts with silica or alumina in sludge to produce hydrated products such as C–S–H and C–A–H [11].

Immobilization of heavy metals with phosphate-containing apatite minerals [$(Ca_5(PO_4)_3X)$ (X = halide, hydroxyl)] has been also considered to be effective. The formation of secondary phosphates can precipitate and remain stable over a wide range of geochemical conditions [12,13]. Hydroxyapatite (HAP) has been reported to rapidly and completely immobilize Pb by the formation of hydroxypyromorphite [$Pb_{10}(PO_4)_6(OH)_2$] [12] and also to be effective in the immobilization of Zn and Cu in soils [14,15].

Iron sulfate ($FeSO_4$) has been used to immobilize Pb, Zn, Cu, and Cd in soil [16] as well as to reduce Cr(VI) to Cr(III) for the Cr remediation since Cr(III) is more stable and less soluble than Cr(VI) [17,18]. Thus, conversion of the Cr(VI) to Cr(III) is recommended to enhance Cr immobilization efficiency by S/S treatment. In addition, $FeSO_4$ is not to interfere with cement in the S/S treatment. But more information is needed to treat the tannery sludge containing high level of chromium and other heavy metals by S/S process with (1) $FeSO_4$ alone and (2) $FeSO_4$ in combination of other binders.

The objectives of this study were as follows: (1) to evaluate the effects of charring temperatures (350, 400, 450, 500, and 550°C), amendment of various binders ($FeSO_4$, lime, cement, HAP, and ladle slag) and aging on the immobilization of heavy metals such as Cr, Pb, Ni, Zn, and Cu in the TSCs and (2) to investigate the microstructure characteristics of dewatered tannery sludge (raw tannery sludge hereafter), TSCs and binder amended TSCs by X-ray diffraction (XRD), energy dispersive X-ray spectrometer (EDS) and scanning electron microscope (SEM) analyses.

2. Materials and methods

2.1. Preparation of TSCs

The raw tannery sludge was obtained from a local tannery industry located in Busan, Korea. The TSCs were prepared by charring the sludge at high temperatures: 350°C (TSC350), 400°C (TSC450), 450°C (TSC450), 500°C (TSC500), and 550°C (TSC550) under oxygen-depleted conditions using a pilot-scale charring process (500 kg/d) at Korea Dyeing Technology Center in Daegu, Korea. The sludge charring process is reported in detail elsewhere [19]. After charring, the TSCs were cooled at room temperature, air-dried, ground, sieved through 600-μm mesh (sieve #30), mixed in a tumbler for homogenization and kept in air-tight containers prior to use.

2.2. Binders

Iron sulfate ($FeSO_4$) (Duksan Chemical Co., Korea, >98%), ordinary Portland cement (OPC, Type I, Hanil Cement Co., Korea), lime ($Ca(OH)_2$, 170 mesh, Chungmoo Chemical Co., Korea, >95%), hydroxyapatite (HAP, Sigma-Aldrich Co., Korea), and ladle slag (POSCO, Pohang, Korea) were used as binders for the immobilization of heavy metals. The binders were ground into fine powder, sieved through 212-μm mesh and then stored in air-tight containers before use.

2.3. Immobilization of heavy metals

The effect of single-binder (i.e. $FeSO_4$ alone) amendment on the Cr immobilization was investigated. About 0.05 or 0.1 g of $FeSO_4$ powder was added into 50-mL polycarbonate vial (Nalgene Co.) containing 1.0 g of TSC and then mixed thoroughly using a vortex mixer (IKA® MS1 mini-shaker). After mixing, the water content of the mixture was adjusted to 50%

(w/w) by adding distilled and deionized (DI) water and then allowed to stand still for one day at room temperature. For binary-binder experiments, 0.05 g of $FeSO_4$ and 0.1 g of the additional binder (cement, lime, HAP or ladle slag) were amended with 1.0 g of TSC. The binary-binder experiments were conducted in the same way as the single-binder experiments. The effect of aging (i.e. 1, 7, and 30 d) on the immobilization of heavy metals in the TSCs was also investigated using the same binder dosage (i.e. 0.05 g of $FeSO_4$ + 0.1 g of the additional binder such as cement, lime, HAP or ladle slag). All experiments were conducted in duplicate.

2.4. Extraction procedures

Background concentrations of heavy metals in the raw tannery sludge and the TSCs were determined using a microwave digestion system (MARS 5, CEM Corp., Matthews, NC, USA) using the US EPA SW-846 method 3051 [20]. Ten milliliters of nitric acid (HNO_3, 65%) was placed in an Omni® vessel containing 0.5 g of TSC, digested in the microwave at 175˚C for 10 min and then cooled down. After cooling, the digest was centrifuged (Union 32R, Hanil Science Industrial Co. Ltd., Korea) for 30 min at 1,200 g. After centrifugation, the supernatants were filtered through the 0.20-μm syringe filter (Whatman, cellulose nitrate membrane filter, $\phi = 25$ mm) and then analyzed by an inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer, 2100DV).

Immobilization efficiencies of the heavy metals after the single- and binary-binder amendments were evaluated by the toxicity characterization leaching procedure (TCLP, USEPA 2007, SW-846, Method 1311) [21]. The TCLP solution was prepared by dissolving 5.7 mL of glacial acetic acid (99%) in 1 L of DI water. The pH of the extracting solution was 2.88 ± 0.05 [21]. For the TCLP test, 20 mL of the acetic acid solution was added into 50 mL polycarbonate vial (Nalgene Co.) containing 1.0 g of TSC (solid/liquid = 1:20, W/V). The sealed samples were agitated on a horizontal orbital shaker (DR 302 DF, Daeryun Scientific Co., Korea) for 24 h at 200 rpm and then centrifuged for 30 min at 1,200 g. After centrifugation, the supernatants were filtered through the syringe filter and then analyzed by the ICP-OES.

The pH of TSC was measured using a pH meter (Orion 290A, Thermo Electron Corp., USA) at a solid/water ratio of 1:5 [22].

2.5. Microstructural analyses

The surface characteristics of the TSCs were investigated using a SEM (scanning electron microscopy, S-4300, Hitachi, Japan,) to analyze the changes in shape, size, and morphology before and after heavy metal immobilization. Mineral compositions of the binders were also investigated using an X-ray fluorescence (XRF, PW2400, Philips Electronic Instruments, Inc., the Netherlands) and identified by an XRD analysis using an X-ray diffractometer (Rigaku, D/Max-2500, the Netherlands). The EDS peaks (energy dispersive X-ray spectroscopy, S-4800, Hitachi, Japan) were analyzed to identify the chemical compositions. The BET (Brunauer–Emmet–Teller) surface area was measured by a BET analyzer (Micromeritics, ASAP2010, USA).

3. Results and discussion

3.1. Physicochemical properties of TSCs and the binders

Background concentrations of heavy metals in the raw tannery sludge and TSCs were determined by the microwave-assisted acid digestion (Fig. 1(a)) and TCLP-extractable concentrations of heavy metals (Pb,

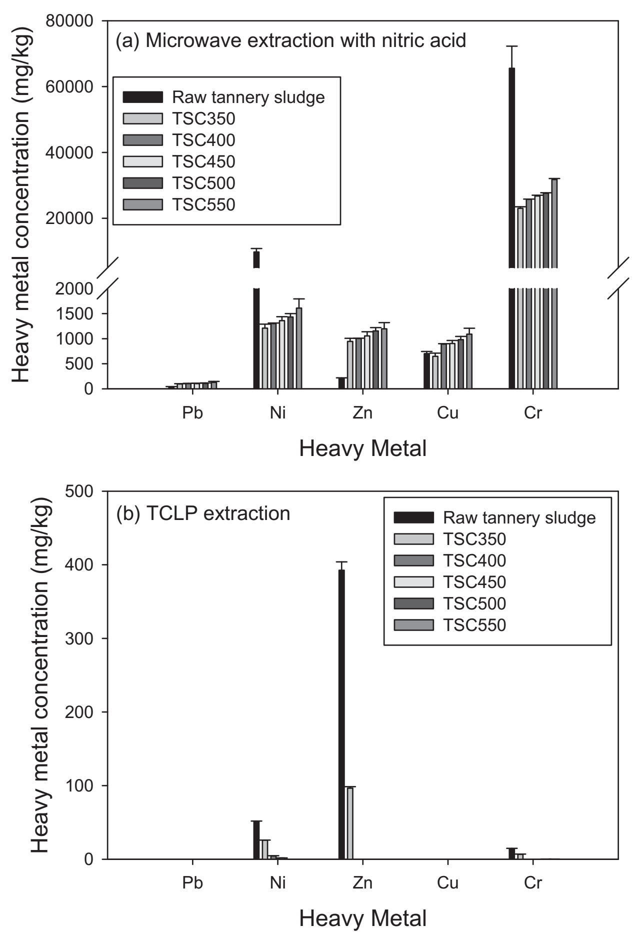

Fig. 1. Heavy metal concentration in TSC: (a) microwave extraction with nitric acid and (b) TCLP extraction.

Ni, Zn, Cu, and Cr) in the TSCs were measured by TCLP extraction (Fig. 1(b)), respectively. The raw tannery sludge was mainly contaminated with Cr followed by Ni, Cu, Zn, and Pb as shown in Fig. 1(a). In the raw tannery sludge, the background concentrations of Cr (65,560 mg/kg) and Ni (9,786 mg/kg) were higher than those of Pb (43.0 mg/kg), Zn (206.9 mg/kg), and Cu (700.4 mg/kg). After charring, all heavy metal concentrations except for Pb remarkably decreased as compared to those in the raw sludge (Fig. 1(a)). For the TSCs, the pseudo-total heavy metal concentrations increased as the charring temperature increased above 350℃.

The TCLP-extractable concentrations of Zn, Ni, and Cr from the raw tannery sludge were 392.5, 51.30, and 14.36 mg/kg, respectively. After charring at 350℃, the TCLP-extractable concentrations of Zn, Ni, and Cr were reduced to 96.6, 25.8, and 6.61 mg/kg, respectively. As the charring temperature increased above 400℃, the TCLP-extractable concentrations of Zn, Ni, and Cr were negligible (Fig. 1(b)). The results of technical analyses of the raw tannery sludge and TSCs were listed in Table 1. The ash content in TSCs increased with the charring temperature, but the volatile matter (VM) and fixed carbon (FC) contents decreased. The TCLP-extractable concentrations of heavy metals in the TSCs decreased with increasing ash content and decreasing VM content (see Fig. 1(b) and Table 1). The BET surface areas of TSCs were 1.695 m^2/g for TSC350, 4.398 m^2/g for TSC450, and 6.875 m^2/g for TSC550, respectively, indicating that BET surface area increased with the charring temperature.

The chemical compositions of the raw tannery sludge, TSCs and binders determined by XRF analyses are listed in Table 2. Raw tannery sludge had high

Table 1
Technical analysis of tannery sludge

Materials	Technical analysis (%)				Element (%)				
	Water	VM[a]	FC[b]	Ash	C	H	O	N	Cl
Raw tannery sludge	76.40	74.70	2.18	23.12	42.13	5.59	21.27	4.74	0.98
TSC350	14.30	53.96	6.14	39.90	38.48	3.71	9.60	4.05	1.42
TSC450	12.10	35.28	4.71	60.01	23.52	1.41	5.20	3.86	2.11
TSC550	13.80	33.36	3.65	62.99	22.86	1.26	3.22	3.39	2.13

[a]VM: Volatile matter.
[b]FC: Fixed carbon.

Table 2
XRF analyses of raw tannery sludge, TSCs, and binders

Chemical composition (%)	Raw tannery sludge	TSCs			Binders			
		TSC350	TSC450	TSC550	Lime	Cement	Ladle slag	HAP
MgO	ND[a]	ND	ND	ND	0.88	2.37	2.82	0.49
Al_2O_3	0.49	1.03	0.52	0.59	0.28	3.60	22.5	ND
SiO_2	1.81	1.28	0.92	0.95	0.82	17.4	11.1	ND
P_2O_5	ND	0.35	0.18	0.21	ND	0.09	0.05	40.1
SO_3	1.93	2.27	2.09	1.28	0.14	3.26	0.82	ND
K_2O	0.17	0.19	0.21	ND	0.08	1.46	0.15	ND
CaO	13.1	11.4	20.6	10.4	97.2	67.3	57.9	59.4
TiO_2	1.09	ND	ND	ND	ND	0.29	0.24	ND
MnO	0.48	ND	ND	ND	ND	ND	1.42	ND
Fe_2O_3	37.2	70.3	65.7	73.37	0.52	3.99	2.95	ND
ZnO	7.09	0.87	0.79	0.96	ND	0.07	ND	ND
Cr_2O_3	35.9	11.4	7.99	11.8	ND	ND	ND	ND
SrO	ND	ND	ND	ND	ND	0.12	ND	ND
CuO	0.52	ND	ND	ND	ND	ND	ND	ND
Cl	0.23	ND	ND	ND	ND	ND	ND	ND

[a]ND: Not detected.

content of Cr_2O_3 (35.9%) and Fe_2O_3 (37.2%). All TSCs had high contents of Fe_2O_3 (65–73%) and CaO (10–20%). The CaO content was the highest (about 20%) at 450℃ of the charring temperature as compared to those (about 10%) at 350 and 550℃. The dominant CaO content in the binders was in the order of lime (97.2%) > cement (67.3%) > HAP (59.4%) > ladle slag (57.9%). Cement and ladle slag also had high contents of SiO_2 (17.4 and 11.1%, respectively) and Al_2O_3 (3.60 and 22.5%, respectively). This indicates that the main immobilization mechanisms of heavy metals with cement and ladle slag would be due to the pozzolanic reaction where C–S–H and C–A–H can be formed in the presence of Ca, Si, and Al oxides [11]. HAP had no Al_2O_3 and SiO_2 contents, but high P_2O_5 content (32.9%). This indicates that metal immobilization by HAP occurs by the formation of pyromorphite or metal precipitates [23].

Fig. 2 shows the microstructures of raw tannery sludge and TSCs observed by SEM. Compared to the raw tannery sludge (Fig. 2(a)), some bright materials were observed on the surface of the TSCs charred at 350–550℃ (Fig. 2(b)–(f)). Fig. 3 shows the XRD analyses of the raw sludge and TSCs. The peak height (intensity, ~2,500) of the Ca crystalline, such as calcite ($CaCO_3$) and calcium carbide (CaC_2), in the TSCs was higher than those (~300) in the raw tannery sludge, especially calcite peaks at about 29˚ of 2θ in the TSC450, TSC500, and TSC550. As shown in Fig. 1(b), no appreciable TCLP-extractable concentrations of

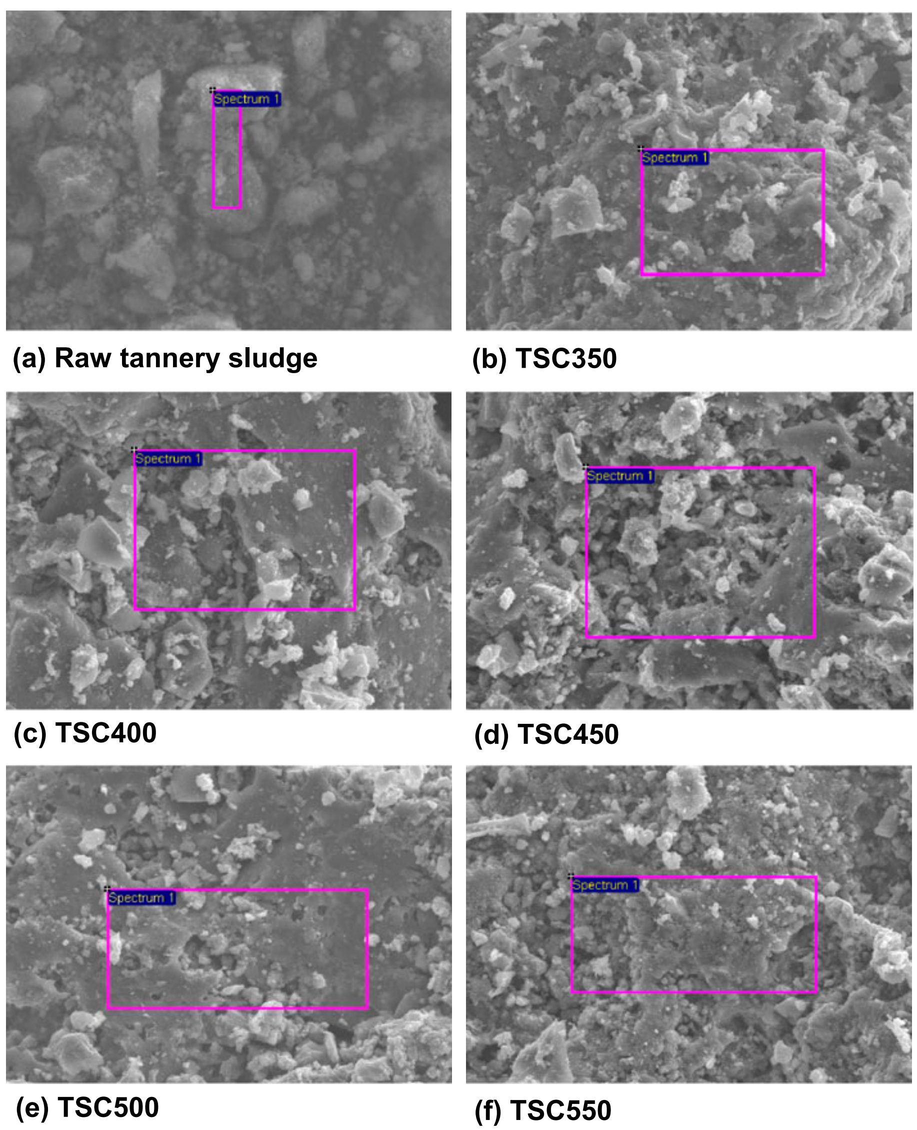

Fig. 2. SEM photographs of (a) raw tannery sludge, (b) TSC350, (c) TSC400, (d) TSC450, (e) TSC500, and (f) TSC550.

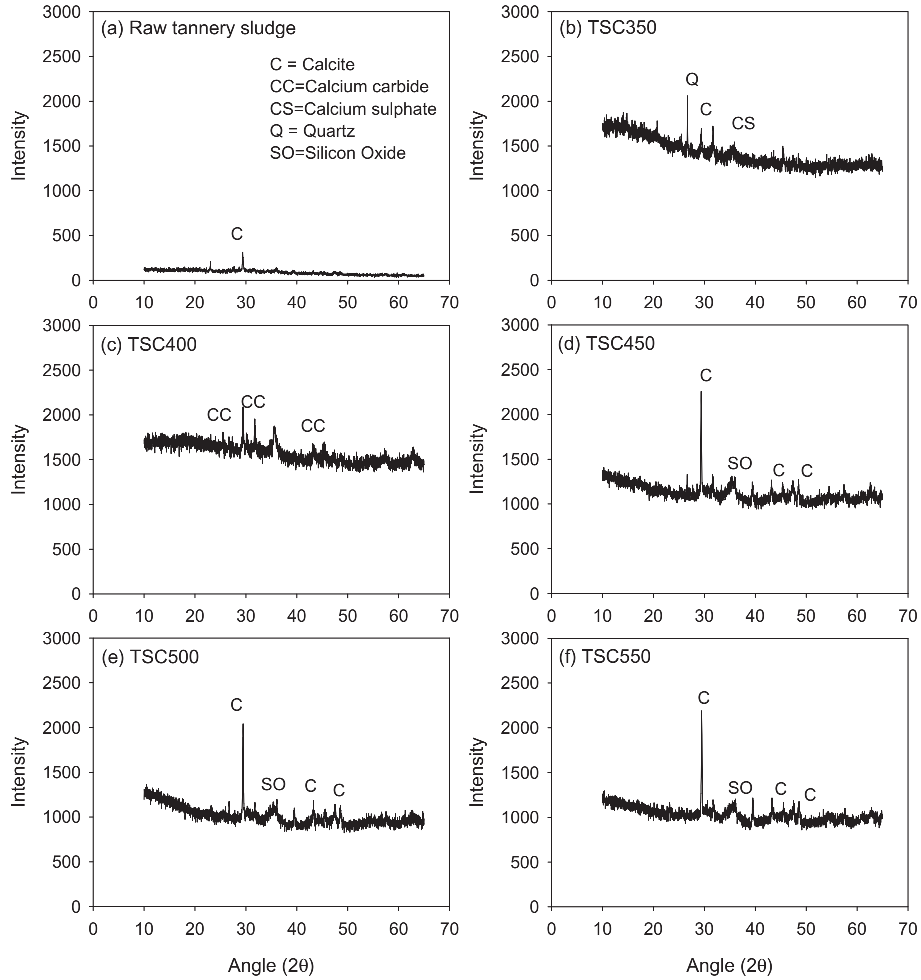

Fig. 3. XRD analyses of (a) raw tannery sludge, (b) TSC350, (c) TSC400, (d) TSC450, (e) TSC500, and (f) TSC550.

heavy metals including Cr were detected in the TSC450, TSC500, and TSC550 even though very high concentrations of heavy metals were extracted by microwave digestion with nitric acid (Fig. 1(a)), which were mainly due to high level of calcite present in the TSC450, TSC500, and TSC550. The calcite in the TSCs can bind the heavy metals, thereby reducing TCLP-extractable metal concentrations.

3.2. *Cr and other heavy metals Immobilization by $FeSO_4$ (1-d aging)*

The immobilization efficiency of Cr by $FeSO_4$ addition after 1-d aging was evaluated by TCLP (Fig. 4(a)). The extractable Cr concentrations from the control TSCs (no binder added) were 6.61 mg/kg for TSC350, 1.08 mg/kg for TSC400, 0.10 mg/kg for TSC450, 0.15 mg/kg for TSC500 and 0.23 mg/kg for TSC550, respectively. It was clear that the TCLP-extractable Cr concentrations in the TSCs sharply decreased as the charring temperature increased from 350 to 450℃, but slightly increased as the temperature increased above 450℃. Therefore, the optimum charring temperature to minimize the TCLP-extractable Cr concentrations from the TSCs was 450℃.

$FeSO_4$ was used as a Fe(II) source for Cr immobilization because Cr(VI) is strong oxidant and reacts rapidly with Fe(II) [24,25]. The chromate ($Cr_2O_7^{2-}$) was transformed to chromium oxide (Cr_2O_3) when treated with Fe(II). The reaction between Fe(II) and Cr(VI) is represented by Eq. (1) [17].

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \quad (1)$$

Cheng et al. [17] reported that the ferrous iron such as $FeCl_2$ or $FeSO_4$ was highly effective (efficiency >70%) in reducing Cr(VI) from alkaline soils. In this study, above 60 and 85% of the total amount of Cr

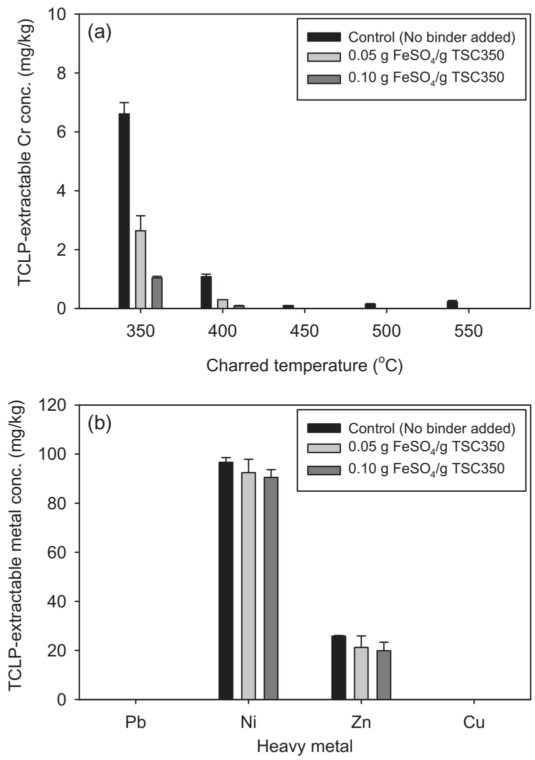

Fig. 4. TCLP extractable concentrations of (a) Cr from TSCs and (b) Pb, Ni, Zn, and Cu from TSC350 after immobilization by $FeSO_4$.

was immobilized by the amendment of 0.05 and 0.10 g of $FeSO_4$ per 1 g of dried TSC350, respectively. The Cr immobilization efficiency was nearly 100% for TSC450, TSC500, and TSC550, indicating that the Cr in the TSCs prepared at temperature above 450˚C was completely immobilized by $FeSO_4$ addition. Since TSC350 requires less energy than the other TSCs prepared at higher temperature (i.e. >350˚C), the Cr immobilization of TSC350 would be more economically feasible.

The immobilization efficiencies of the other heavy metals (Pb, Ni, Zn, and Cu) were evaluated by TCLP after $FeSO_4$ amendment (Fig. 4(b)). The TCLP-extractable Pb, Ni, Zn, and Cu were not meaningful (very low concentration) at the temperature above 350˚C. Thus, the further immobilization by $FeSO_4$ for other heavy metals was conducted for TSC350 only. At 0.05 g $FeSO_4$/g dry-TSC350, the immobilization efficiencies of Zn and Ni were only 4 and 16%, respectively. The immobilization efficiencies of Ni and Zn were not further improved as the $FeSO_4$ dosage increased to 0.1 g $FeSO_4$/g dry TSC350, indicating that $FeSO_4$ was not efficient for immobilizing other heavy metals (Ni and Zn). Therefore, binary binders ($FeSO_4$ + additional binder) were used to improve Ni and Zn immobilizations in TSC350.

3.3. Heavy metals immobilization in TSC350 by binary binders (1-d aging)

In order to enhance the immobilization efficiency of heavy metals (especially, Ni and Zn) in TSC350, binary binders consisted of 0.05 g $FeSO_4$ + 0.1 g of cement, HAP, lime or ladle slag g^{-1} dry-TSC350 were used. The immobilization efficiency evaluated by TCLP was shown in Fig. 5. The Ni immobilization efficiency for TSC350 was in the order of $FeSO_4$ + lime (100%, 0.0 mg/kg) > $FeSO_4$ + cement (95%, 1.28 mg/kg) > $FeSO_4$ + ladle slag (84%, 4.01 mg/kg) > $FeSO_4$ + HAP (25%, 19.21 mg/kg). Fang and Wong [7] reported that Ni immobilization efficiency was 80–90% in 0.63–1.63% lime-amended sewage sludge. The Zn immobilization efficiency was in the order of $FeSO_4$ + lime (100%, 0.0 mg/kg) > $FeSO_4$ + cement (98.4%, 1.46 mg/kg) > $FeSO_4$ + ladle slag (92.7%, 7.05 mg/kg) > $FeSO_4$ + HAP (54.5%, 43.93 mg/kg). Binary binders improved the Zn immobilization efficiency by 36–82%, and Ni by 7.1–82%. $FeSO_4$ + lime/cement/ladle slag were more efficient than $FeSO_4$ + HAP in the immobilization of Ni and Zn in the TSC350.

The improved heavy metal immobilization using binary-binder addition is attributed to: (1) calcite formation by the additional binders [26] and (2) the formation of metal hydroxide on the C–S–H phase [27]. Calcite formed during the charring and addition of cement/lime/ladle slag sealed the pore of the TSCs, thus the leaching of heavy metals was blocked [26]. Lin et al. [28] also reported that the calcium in the sludge ash and lime can form either C–S–H or C–A–H during hydration due to the pozzolanic reaction.

The immobilization of heavy metals by HAP is due to pyromorphite formation. Lower et al. [23] reported that the HAP dissociates into calcium and phosphate, and then the phosphate reacts with

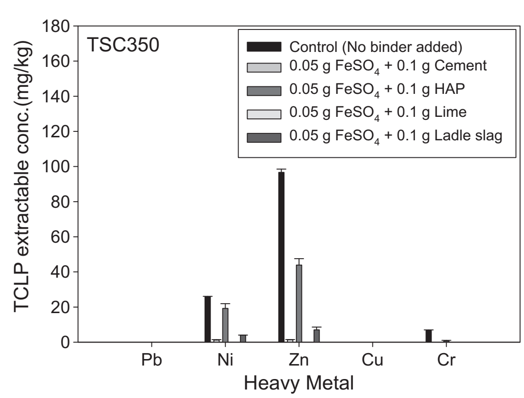

Fig. 5. TCLP extractable concentrations of heavy metals from TSC350 after immobilization by $FeSO_4$ + cement, HAP, lime or ladle slag.

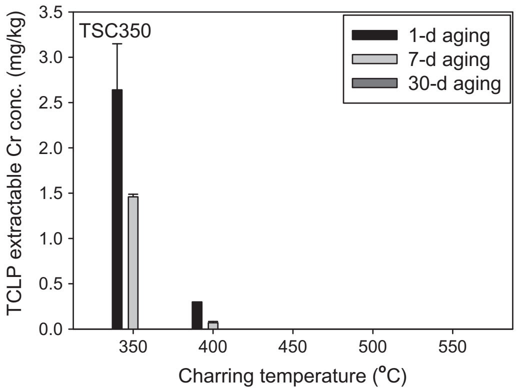

Fig. 6. Effect of aging on the TCLP extractable Cr concentration from TSCs after immobilization by $FeSO_4$.

dissolved Pb to form precipitate of hydroxylpyromorphite. The dissociation of HAP and the reaction of phosphate with dissolved Pb to form hydroxylpyromorphite are represented by Eqs. (2) and (3), respectively.

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

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

Addition of binary binders (i.e. 0.05 g of $FeSO_4$ + 0.1 g of cement, lime, HAP or ladle slag) almost completely immobilized Cr (Fig. 5) and much more efficient than single binder (i.e. $FeSO_4$ alone) amendment. This is due to further immobilization by additional Ca^{2+} derived from the added cement, HAP, lime or ladle slag and noninterference of $FeSO_4$ into immobilization of heavy metals by the additional binders. Wang and Vipulanandan [18] reported that the overall treatment efficiency for Cr(VI) was 99% when Cr(VI) (7,000 mg/kg) spiked soil was treated by 10% $FeCl_2$ followed by a cement-based S/S. In this reaction, the chromate CrO_4^- was transformed to a chromium oxide (Cr_2O_3) by Fe(II) and the chromium oxide (Cr_2O_3) was further converted to $Cr(OH)_3$ when cement was added [17]. In addition, Wang and Vipulanandan [29] also demonstrated that the Cr immobilization by Ca^{2+} addition occurs by the formation of a complex calcium chromate ($CaCrO_4$) with low solubility at pH 12. In this study, pH increased after immobilization using binary binders as compared to using $FeSO_4$ only (see Section 3.5 for more discussion).

3.4. Effect of aging on Cr immobilization by $FeSO_4$ alone

The effect of aging on the Cr immobilization by $FeSO_4$ alone in the five different TSCs was investigated (Fig. 6). The TCLP-extractable Cr concentrations were detected only in TSC350 (2.6 mg/kg) and TSC400 (0.3 mg/kg) but not in TSC450, TSC500, and

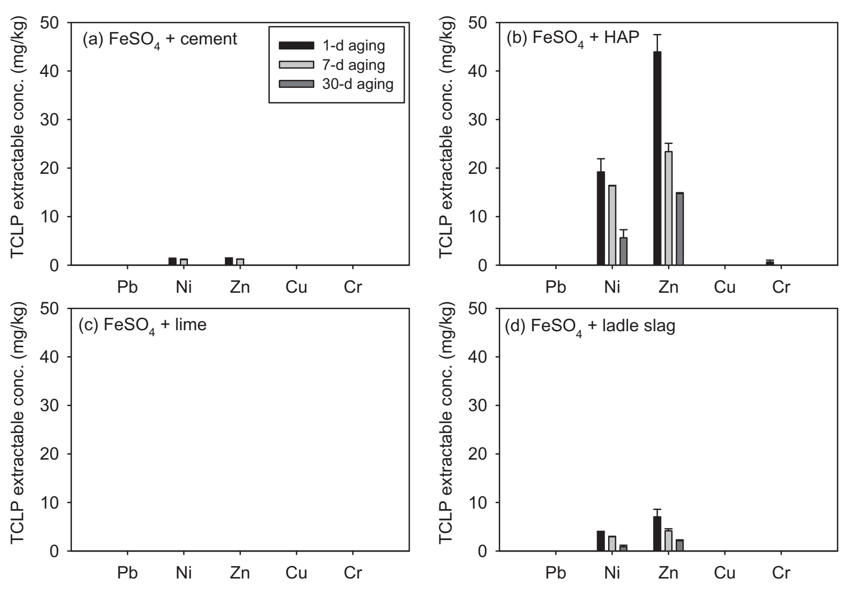

Fig. 7. Effect of aging on the TCLP extractable concentrations of heavy metals from TSC350 immobilized by (a) $FeSO_4$ + cement, (b) $FeSO_4$ + HAP, (c) $FeSO_4$ + lime and (d) $FeSO_4$ + ladle slag.

TSC550. Fig. 6 also shows that the TCLP-extractable Cr sharply decreased, as aging time increased.

3.5. *Effect of aging on metal immobilization by binary binders*

To evaluate the effect of aging (1, 7, and 30 d) on the immobilization of heavy metals by binary binders, the leaching potential of Cr and the heavy metals was evaluated by TCLP only for TSC350 and depicted in Fig. 7. In all binary-binders-amended TSC350, the TCLP-extractable Ni and Zn concentrations decreased with aging except $FeSO_4$ + lime-amended TSC350. The extractable Zn decreased from 96.65 mg/kg (control, no binder amended TSC350) to 1.46, 1.22, and 0.00 mg/kg, in $FeSO_4$ + cement amended TSC350 after 1-, 7-, and 30-d aging (Fig. 7), respectively. The continuous utilization of Al_2O_3 and SiO_2 in the pozzolanic reaction with CaO in the 0.05 g $FeSO_4$ + 0.1 g cement, 0.05 g $FeSO_4$ + 0.1 g ladle slag and 0.05 g $FeSO_4$ + 0.1 g lime-amended TSCs during aging may cause reduced TCLP-extractable Zn, Ni, and Cr concentrations (Table 3). Similarly, the extractable Ni decreased from 25.84 mg/kg to 1.28, 1.14, and 0.00 mg/kg, respectively. The results indicate that the immobilization efficiency increased as the contact time increased from 1 to 30 d. In $FeSO_4$ + lime amendment, no heavy metals were extracted from TSC350 (see Fig. 7(c)) indicating that all heavy metals were completely immobilized. Among the binary-binders, $FeSO_4$ + HAP was not efficient. This is attributed to the difference in the immobilization mechanisms; pozzolanic reaction occurred in the cement, ladle slag and lime amendments vs. pyromorphite or metal precipitate formation in HAP amendment. The pozzolanic reaction cannot occur in the HAP amended TSC350 due to the absence of SiO_2 and Al_2O_3. This indicates that the heavy metals immobilization by the pozzolanic reaction is more effective than by the pyromorphite formation.

The pH levels of the untreated TSCs, $FeSO_4$-amended TSCs and binary-binder amended TSCs are presented in Table 4. The pH of the untreated TSCs increased with the charring temperatures but remained steady at pH 8.68 as the charring temperature increased above 500°C. The pH of $FeSO_4$ amended TSCs (0.05 g $FeSO_4$/g TSC) after 1-d immobilization was reduced to 5.84 (TSC350), 6.34 (TSC400), 7.09 (TSC450), 7.24 (TSC500), and 7.30 (TSC550), respectively. As expected, the pH of TSCs increased in the binary-binder amended TSCs (i.e. 0.05 g $FeSO_4$ + 0.1 g cement/lime/ladle slag/HAP per g TSC). This is because, when the carbonate is dis-

Table 3
XRF analysis of TSC350 after immobilization (aging = 1 and 7 d)

Chemical composition (%)	1-d aging				7-d aging			
	0.05 g $FeSO_4$ + 0.1 g lime[a]	0.05 g $FeSO_4$ + 0.1 g cement	0.05 g $FeSO_4$ + 0.1 g ladle slag	0.05 g $FeSO_4$ + 0.1 g HAP	0.05 g $FeSO_4$ + 0.1 g lime	0.05 g $FeSO_4$ + 0.1 g cement	0.05 g $FeSO_4$ + 0.1 g ladle slag	0.05 g $FeSO_4$ + 0.1 g HAP
Al_2O_3	1.37	1.26	1.00	0.58	0.45	0.84	2.33	0.41
SiO_2	1.15	1.11	3.27	0.72	0.81	2.68	1.70	0.58
P_2O_5	0.17	0.15	0.16	1.29	0.15	0.17	0.23	1.23
SO_3	2.22	2.13	2.31	1.92	1.93	2.12	2.06	1.67
Cl	0.37	0.41	0.46	0.35	0.37	0.32	0.36	0.28
K_2O	0.19	ND[b]	0.35	0.15	ND	0.34	0.18	ND
CaO	17.97	18.54	20.39	17.92	18.09	19.76	17.11	18.34
TiO_2	0.27	ND	0.32	0.19	ND	0.30	0.30	ND
Cr_2O_3	9.55	8.99	9.22	6.48	9.83	9.29	8.40	6.35
Fe_2O_3	66.08	66.61	61.83	35.29	67.64	63.48	66.59	37.02
ZnO	0.71	0.79	0.70	35.11	0.73	0.69	0.74	34.13

[a]Amended per g of TSC350.
[b]ND: Not detected.

Table 4
pH of TSCs and binder-amended TSCs (aging = 1 d)

TSCs	pH					
		Binders				
	Control (no binder added)	0.05 g $FeSO_4$ alone	0.05 g $FeSO_4$ + 0.1 g cement[a]	0.05 g $FeSO_4$ + 0.1 g lime[a]	0.05 g $FeSO_4$ + 0.1 g ladle slag[a]	0.05 g $FeSO_4$ + 0.1 g HAP[a]
TSC350	7.12	5.84	10.37	10.53	9.62	7.07
TSC400	7.27	6.34	11.17	11.60	10.35	8.24
TSC450	8.67	7.09	11.55	12.41	10.95	8.73
TSC500	8.68	7.24	11.84	12.51	11.17	9.01
TSC550	8.68	7.30	11.96	12.28	11.32	9.17

[a]Amended per g of TSCs.

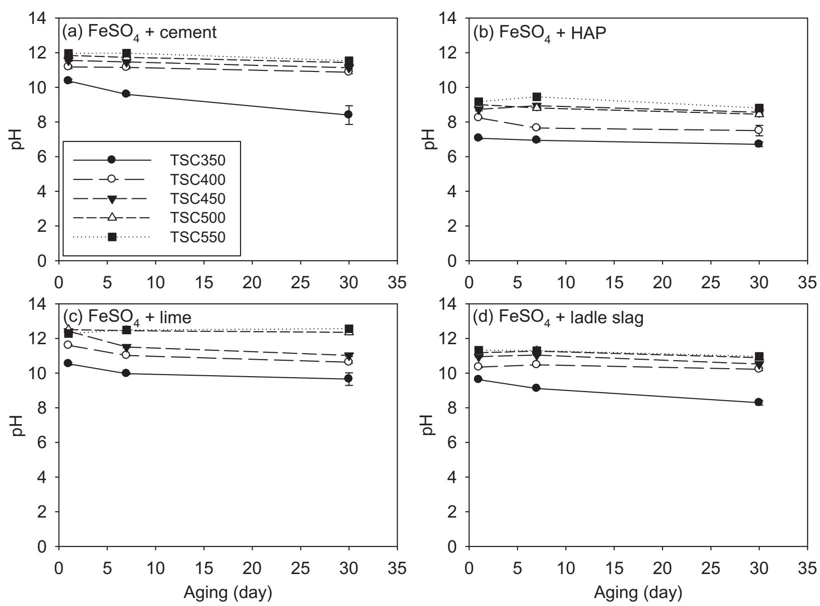

Fig. 8. Effect of aging on the pH of TSCs after immobilization by (a) $FeSO_4$ + cement, (b) $FeSO_4$ + HAP, (c) $FeSO_4$ + lime, and (d) $FeSO_4$ + ladle slag.

sociated from the calcium carbonate, some of the hydrogen ions changed into water and carbon dioxide (CO_2) and the reduced H^+ concentration increases the pH [14]. The pH values were in the order of $FeSO_4$ + lime > $FeSO_4$ + cement > $FeSO_4$ + ladle slag >$FeSO_4$ + HAP after 1-d aging (Fig. 8). Dissolution of CaO present in cement, lime, and ladle slag (Table 3) into water is responsible for the order of pH values. The order of pH values was corresponding to the order of CaO content (lime > cement > ladle slag) except HAP which contains also high level of P_2O_5 (40.1%) is expected to play a role as pH buffer.

4. Conclusion

The immobilization of the heavy metals (Pb, Ni, Zn, Cu, and Cr) in the TSCs prepared at high temperatures (350, 400, 450, 500, and 550˚C) was carried out by both single ($FeSO_4$) and binary-binder ($FeSO_4$ + cement, $FeSO_4$ + Lime, $FeSO_4$ + HAP, and $FeSO_4$ + ladle slag) amendments. The immobilization efficiencies were evaluated by TCLP after 1-d, 7-d, and 30-d aging.

After immobilization, the TCLP-extractable heavy metal concentrations decreased with charring temperatures, consistent with the increase in ash content and decrease in VM content in the TSCs. As the charring temperature increased above 450°C, less amount of heavy metals were extracted by the TCLP. For Cr immobilization, 0.05 g $FeSO_4$ g^{-1} dry TSC was highly effective (2.6, 0.30, 0.0, 0.0, and 0.0 mg/kg for TSC350, 400, 450, 500, and 550, respectively). The Cr immobilization by $FeSO_4$ amendment was attributed to the reduction of Cr^{6+} to Cr^{3+}. Among the four binary binders, $FeSO_4$ + lime showed the best immobilization efficiency of Cr, Ni, and Zn. Immobilization efficiency was higher for the binders (cement, lime, and ladle slag) containing higher CaO and SiO_2 contents than that for HAP containing less CaO and SiO_2. The retention of heavy metals in the binders after hydration (the hydration reaction starts after the addition of water to the binder and sludge) could be due to the combination of (1) calcite formation by the additional binders and (2) the formation of metal hydroxides on the C–S–H phase. In the binary binder treatments, aging or contact time was critical in the immobilization of heavy metals in TSC350. The heavy metals immobilization efficiency increased with aging. The pH of the immobilized samples decreased with aging. These results implicate that the S/S using binary-binders such as $FeSO_4$ + cement/lime/ladle slag are useful in the immobilization of heavy metals in TSCs.

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