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ORIGINAL ARTICLE

An assessment of Portland cement, cement kiln dust and Class C fly ash for the immobilization of Zn in contaminated soils

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Abstract Zn-contaminated soils obtained from a steel company in the Republic of Korea were stabilized using Portland cement (PC), cement kiln dust (CKD) and Class C fly ash (FA). The effectiveness of the treatment was evaluated by the United States Environmental Protection Agency toxicity characteristic leaching procedure (TCLP) and the Universal Treatment Standard (UTS) of 4.3 mg/L. X-ray powder diffraction (XRPD) analyses were performed to investigate the crystalline phases associated with Zn immobilization. Scanning electron microscopy (SEM)–energy dispersive X-ray (EDX) analyses were utilized to support the XRPD results. The treatment results showed that the TCLP-Zn concentrations obtained from the 10 wt% PC and 15 wt% CKD treated samples were less than the UTS, after 7 days curing. However, the FA treatment (up to 30 wt%) was not effective in meeting the UTS even after 28 days curing. All PC–CKD treatment combinations were effective in reducing the TCLP-Zn concentrations below the UTS criteria. Moreover, a 20 wt% dose of a PC-FA treatment combination (75/25 PC-FA) was successful in reducing the TCLP-Zn concentrations below 4.3 mg/L after 1 day. The XRPD results showed that ettringite and $Zn_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$ were the possible phases associated with Zn immobilization upon PC and CKD treatment. The SEM–EDX results confirmed the presence of ettringite, while $Zn_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$ was not identified.

Keywords Zinc (Zn) · Stabilization · Portland cement · Cement kiln dust · Fly ash · Toxicity characteristic leaching procedure (TCLP)

Introduction

Zinc (Zn) is listed as priority pollutant by the United States Environmental Protection Agency (USEPA) (Qian et al. 2003). Zn contamination in soils is a serious problem in industrial sites and those in the Republic of Korea require immediate attention.

Stabilization/solidification (S/S) processes have been widely used to treat hazardous wastes containing Zn and other heavy metals (Cocke et al. 1992; Lo et al. 2000; Daniels et al. 2001; Qian et al. 2003). According to the USEPA, S/S is known as a best demonstrated available technology (BDAT) that has been implemented at 57 hazardous wastes (USEPA 1993). Various S/S agents such as Portland cement, lime, fly ash, etc. have been used to immobilize heavy metals in contaminated soils. Moreover, cement-based S/S technique is mostly appropriate for heavy metal contaminated wastes, sludge and soils (Conner 1990; Batchelor 2006). The S/S technique involves the mixing of contaminated soils with pozzolanic agents to reduce the leachability of the contaminant. Then, the treated hazardous materials can be converted into an environmentally acceptable form for use in land disposal or construction (Shi and Fernández-Jiménez 2006).

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In this treatability study, the S/S technique was employed to evaluate the remediation of Zn-contaminated soils. The combination of Type I/II Portland cement (PC), cement kiln dust (CKD) and Class C fly ash (FA) were used to immobilize Zn in the contaminated soils, using curing periods of 1-, 7- and 28-days. The assessment of CKD and FA to immobilize Zn was investigated due to their low cost effectiveness. CKD and FA can be used instead of PC as major stabilizing agents with very low costs (Moon and Dermatas 2007; Moon et al. 2008). Moreover, the costs associated with CKD and FA disposal are high. The challenge of CKD and FA disposal would be minimized if they can be used beneficially for soil stabilization. However, detailed studies in this area are limited and further research is needed to provide a better evaluation of the S/S treatment effectiveness.

In the Zn–H_2O system, $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ are the prevailing Zn species under alkaline pH conditions (Pourbaix 1974). It has been reported that in a Zn-spiked Ordinary Portland cement (OPC) matrix, when sufficient Ca^{2+} ions are present in solution, Zn solubility is controlled by calcium zincate [$CaZn_2(OH)_6 \cdot 2H_2O$] (Yousuf et al. 1992). This precipitate covers cement grains and prevents their further hydration (Cocke and Mollah 1993; Yousuf et al. 1995). Rose et al. (2001) reported that Zn ions at low concentrations can be directly incorporated into calcium silicate hydrate (C-S-H) compounds. The Zn substitution occurs either by replacement of Ca^{2+} or by direct linkage to the end of the silicate chains through Zn–O–Si bonds (Moulin et al. 1999; Rose et al. 2001). Moreover, the formation of $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ and $CaO[Zn(OH)_2] \cdot 2H_2O$ have been reported when the $Zn(OH)_2$ was blended with PC (Qiao et al. 2007).

Ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$] is well known cement phase which has a needle-like morphology (Dermatas 1995). Ettringite forms immediately in normal commercial PC by hydration and reaction between cement compounds and sulfate (Schwiete and Niël 1965). The replacement of Ca^{2+} by Zn^{2+} in the ettringite crystal structure also has been reported (Poon et al. 1985; Bonen and Sarkar 1994).

The purpose of this study was to evaluate the effectiveness of the S/S treatment of Zn-contaminated soils using combinations of PC, CKD and FA. Also, this study was conducted to determine if CKD and FA are suitable as alternative, low cost S/S agents to PC. The effectiveness of S/S treatment was evaluated by the toxicity characteristic leaching procedure (TCLP). As no TCLP regulatory limit has been established for Zn, the USEPA Universal Treatment Standard (UTS) developed as part of the landfill disposal restrictions or 4.3 mg/L (USEPA 1999), was used for comparative purposes. The UTS standard has been utilized in a previous cement-based S/S study to immobilize Zn (Ruiz and Irabien 2004). Mineralogical changes in the treated Zn soils were investigated using X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM)–energy dispersive X-ray (EDX) analyses.

Experimental methodology

Zn-contaminated soils

Zn-contaminated soils were obtained from a steel company in Changwon, Gyeongsangnam-do, Republic of Korea. The soil pH (1:1) was 8.31 according to ASTM D 4980-89 (ASTM 2000) and the contaminated soils were characterized using a particle size analysis system (Sedigraph 5100, USA). The soils were composed of 55.7% sand, 33.8% silt and 10.3% clay. The organic matter content was 0.6%. A total Zn content of 4,973 mg/kg was obtained by total digestion using a 3:1 HCl/HNO_3 solution (aqua regia). The Zn-contaminated soils were air-dried and sieved using #10 mesh (2 mm) for use in this study.

S/S agents

The Type I/II Portland cement and cement kiln dust (CKD) were provided by LaFarge North America (Whitehall, PA, USA). Class C fly ash (FA) was obtained from American Fly Ash Company (Naperville, IL, USA). The physicochemical properties of the S/S agents are presented in Table 1.

Treatment of Zn-contaminated soils

Control samples were prepared at 50% water content without any stabilizing agents and cured for 1 day. Individual doses of PC, CKD and FA ranged from 5 to 30 wt%

Table 1 Physicochemical properties of the PC, CKD and FA

	PC	CKD	FA
Chemical properties			
SiO_2 (dry wt%)	20.4	19.04	38.2
Al_2O_3 (dry wt%)	5.1	6.12	19.8
Fe_2O_3 (dry wt%)	3.2	2.68	5.11
MgO (dry wt%)	3.8	3.81	3.86
CaO (dry wt%)	62.5	55.97	21.4
Na_2O (dry wt%)	–	0.68	2.04
K_2O (dry wt%)	–	3.81	0.65
SO_3 (dry wt%)	2.8	8.96	2.2
Physical properties			
Surface area (m^2/g)	–	–	31
pH (1:1)	12.24	12.73	12.3

at 5 wt% intervals. Select combinations of PC-CKD and PC-FA at the 20 wt% dose level were also utilized to remediate the Zn-contaminated soils, as shown in Table 2.

TCLP tests

All of the untreated and treated samples were subjected to the TCLP tests in accordance with the USEPA method 1311 (USEPA 1992). Specifically, an acetic acid (pH 2.88 ± 0.05) extraction solution was used to leach Zn from the untreated and treated samples, which were tumbled for 18 h at 30 rpm. After tumbling, the TCLP-pH was measured and the leachate was filtered through a 0.4 μm pore-size membrane filter. The soluble Zn concentration was then analyzed using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Optima 7000DV) (PerkinElmer, CT, USA). Sample analyses were conducted in duplicate or in triplicate, and the average value was reported. The average values were reported only if the individual measurements were within an error range of 10%. For QA/QC purposes, two different quality control standards were used every 10 samples.

XRPD analyses

The mineralogical changes upon PC, CKD and Class C FA treatments were analyzed by XRPD. Prior to XRPD analyses, the samples were air-dried and hand-pulverized to pass through a #200 sieve. Step-scanned X-ray diffraction patterns were collected by a Rigaku D/MAX Ultima III. The XRPD analyses were performed at 40 kV and 40 mA using a diffracted beam graphite-monochromator with Cu radiation. The XRPD patterns were collected in the 2θ range of 5^{o}–65^{o} with a step size of 0.02^{o} and a count time of 3 s per step. The qualitative analyses of the XRPD patterns were conducted using the Jade software version 7.1 (MDI 2005) and the powder diffraction file (PDF)-2 reference database from the International Center for Diffraction Data database (ICDD 2002).

Table 2 Treatability matrix for the 20 wt% PC-CKD and PC-FA Zn stabilization/solidification (S/S) study

Blend	PC (wt%)	CKD (wt%)	FA (wt%)	L:S ratio
25/75	5	15	–	0.5
50/50	10	10	–	0.5
75/25	15	5	–	0.5
25/75	5	–	15	0.5
50/50	10	–	10	0.5
75/25	15	–	5	0.5

SEM–EDX analyses

Select XRPD samples were also evaluated by SEM analyses using a Hitachi S-4700 (Hitachi, Japan) equipped with an energy dispersive X-ray spectroscopy (EDX), Energy EX-200 (Horiba, Japan). Prior to SEM analyses, the air-dried samples were coated with platinum (Pt).

Results and discussion

TCLP results

The TCLP-Zn concentrations and the TCLP-pH values upon PC, CKD, FA, PC-CKD and PC-FA treatments are presented in Figs. 1, 2, 3 and 4. The TCLP-Zn concentrations of the control samples (0 wt%), after 1 day of curing, were 44.6 mg/L (Fig. 1).

Upon PC treatment, the TCLP-Zn concentrations were significantly reduced. Similar Zn leaching behavior in cement-based solidified/stabilized waste materials was attained by Li et al. (2001). Specifically, the TCLP-Zn concentration after 1 day of curing was 0.2 mg/L in the 20 wt% PC treatment. Moreover, no TCLP-Zn concentrations were detected at 25 wt% PC or above (Fig. 1). Overall, the TCLP-Zn concentrations from all of the 10 wt% PC treated samples were less than the UTS of 4.3 mg/L, except for the sample cured for 1 day (10.4 mg/L).

Similarly, the TCLP-Zn concentrations upon CKD treatment were greatly reduced. A TCLP-Zn concentration of 3.1 mg/L was observed for the 20 wt% CKD treatment after 1 day of curing (Fig. 2). Moreover, TCLP-Zn concentrations of 1.85 mg/L and 0.6 mg/L were achieved after 1 day of curing at the 25 and 30 wt% CKD dose levels, respectively (Fig. 2). The TCLP-Zn concentrations from 15 wt% CKD treatment met the UTS of 4.3 mg/L after 7 days.

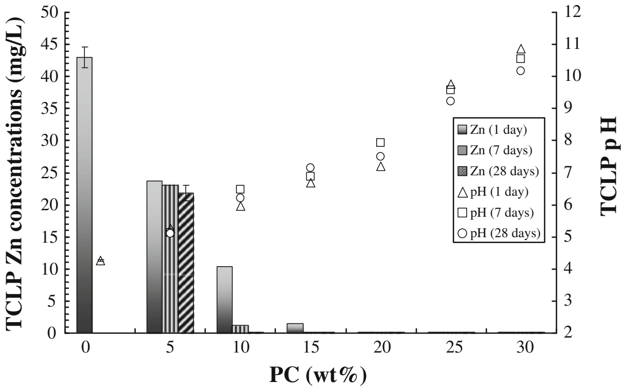

Fig. 1 TCLP-Zn concentrations and pH upon PC treatment

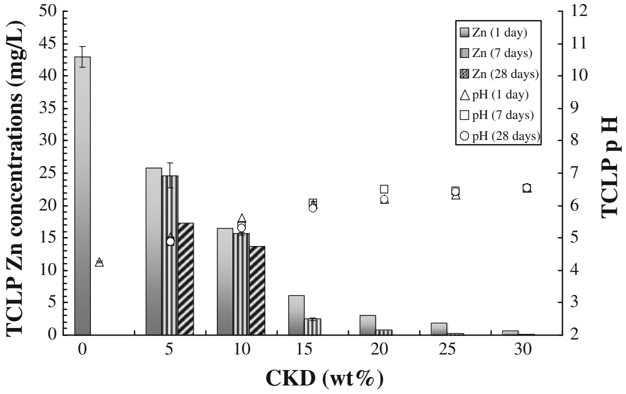

Fig. 2 TCLP-Zn concentrations and pH upon CKD treatment

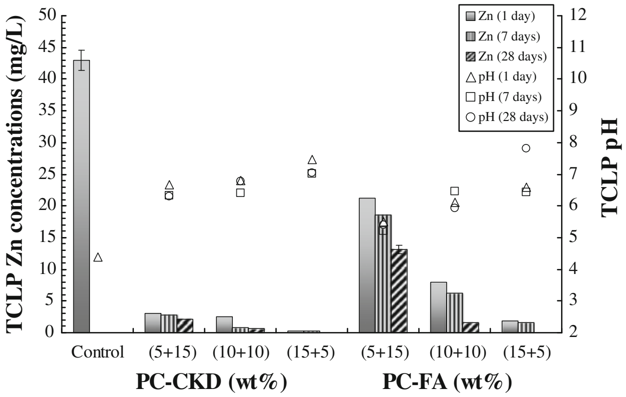

Fig. 3 TCLP-Zn concentrations and pH upon 20 wt% PC-CKD and PC-FA treatments

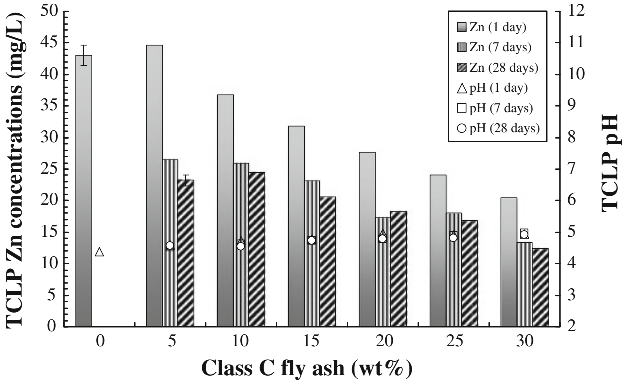

Fig. 4 TCLP-Zn concentrations and pH upon Class C FA treatment

As the PC and CKD doses and curing times increased, the TCLP-Zn concentrations typically decreased. The lowest TCLP-Zn concentrations were observed at 28 days curing. Specifically, TCLP-Zn concentrations less than 1 mg/L were observed for the 15 wt% PC and 20 wt% CKD treatment at 7 days (Figs. 1, 2). The PC-CKD blends were likewise effective (Fig. 3). For example, the 50/50 PC-CKD blend after 28 days of curing attained a leachate concentration less than 1 mg/L (0.62 mg/L). This implies that CKD is a good candidate to effectively immobilize Zn-contaminated soils with lower treatment costs than PC.

The FA treatment was not effective compared to the PC and CKD treatments. Thirty wt% FA achieved the minimum TCLP-Zn consternation of 20.4 mg/L after 1 day of curing. Similar TCLP concentrations were observed after 7 days and 28 days of curing periods (Fig. 4). However, the performance of FA treatment was enhanced in the presence of PC (Fig. 3). Less than 2 mg Zn/L (1.86 mg/L) was observed for the 75/25 PC-FA blend, indicating that FA can be effective when used with PC. Therefore, the addition of only FA is not beneficial for soil stabilization. However, FA with PC addition could be effective at immobilizing Zn in contaminated soils and PC could also be replaced by CKD for lower treatment costs.

The TCLP-pH values increased gradually with increasing pozzolan dose. For instance, the TCLP-pH was greatly increased from 4.5 to 10.9 in the PC treatment. The TCLP-pH ranged from 4.5 to 6.6 increasing doses of CKD. The TCLP-pH was not significantly changed by FA content. The highest pH of 4.9 was observed at 30 wt% FA. This indicates that the 30 wt% FA could not effectively buffer the TCLP solution, limiting immobilization. TCLP-pH values greater than 6.47 and 6.17 for the PC (in the case of the 10 wt% PC sample after 7 days of curing) and CKD (in the case of the 20 wt% CKD sample after 28 days of curing) treatments were required, respectively to pass the UTS limit of 4.3 mg/L, regardless of curing period. For the PC-CKD and PC-FA treatment combinations, the TCLP-pH values greater than 6.3 (25/75 PC-CKD after 28 days of curing) and 5.93 (50/50 PC-FA after 28 days of curing) were required, respectively. Thus, controlling the TCLP-pH above 6.5 is the key to complying with the UTS limit with pH values higher than 6.5.

It has been reported that Zn leaching behavior in the S/S waste matrix was mainly controlled by the alkaline nature and acid buffering capacity of the S/S matrix (Li et al. 2001). Also, the Zn ion can be incorporated into CSH compounds, which is the major phase in hydrated cement (Rose et al. 2001). Therefore, if the TCLP solution is buffered enough by the S/S agents, effective Zn immobilization should be expected.

Overall, the treatment results showed that CKD itself and a combination of PC and FA can be used as alternative cost effective S/S agents instead of PC.

XRPD results

XRPD patterns of the untreated, the 30 wt% PC, 30 wt% CKD and 20 wt% 75/25 PC-CKD blend samples are presented in Fig. 5. In the control, quartz, muscovite, calcite,

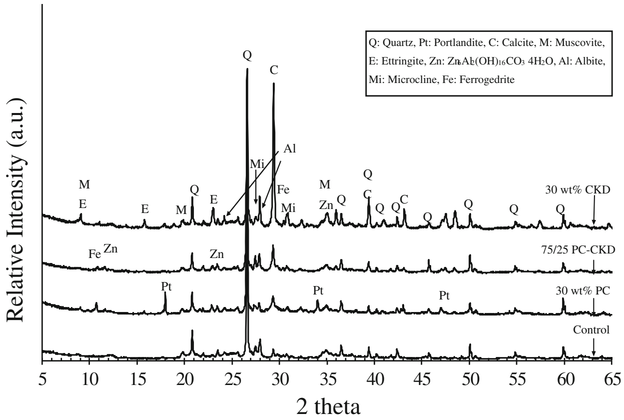

Fig. 5 XRPD patterns for untreated sample and select 28-day cured treatments

albite and microcline were identified as major phases. For the 30 wt% PC treatment, ettringite (PDF# 41-1451), $Zn_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$ (PDF# 38-0486), portlandite (PDF# 44-1481) and ferrogedrite [$Fe_5Al_4Si_6O_{22}(OH)_2$] (PDF# 31-0617) were additionally identified phases. In the 30 wt% CKD treatment, no portlandite, ferrogedrite and $Zn_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$ were observed, ettringite was the dominant phase. In the 75/25 PC-CKD blend treatment, no portlandite was observed. These trends suggest that the Zn in the PC and CKD systems was possibly associated with ettringite and $Zn_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$.

It has been reported that Ca^{2+} in ettringite can be replaced by Zn^{2+} (Poon et al. 1985; Bonen and Sarkar 1994). Moreover, $Zn_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$ has been reported in a PC blend with $Zn(OH)_2$ (Qiao et al. 2007). However, the formation of $CaO(Zn(OH)_2){\cdot}2H_2O$ in the same blend reported by Qiao et al. (2007) was not identified. Also, no calcium zincate [$CaZn_2(OH)_6{\cdot}2H_2O$] reported by Yousuf et al. (1992) was identified in our diffractograms.

SEM–EDX results

The SEM micrographs of the control and select treatments cured for 28 days are presented in Fig. 6. No ettringite was identified in the control (Fig. 6a). In Fig. 6b, c and d, needle-like crystals are ubiquitous, confirming the presence

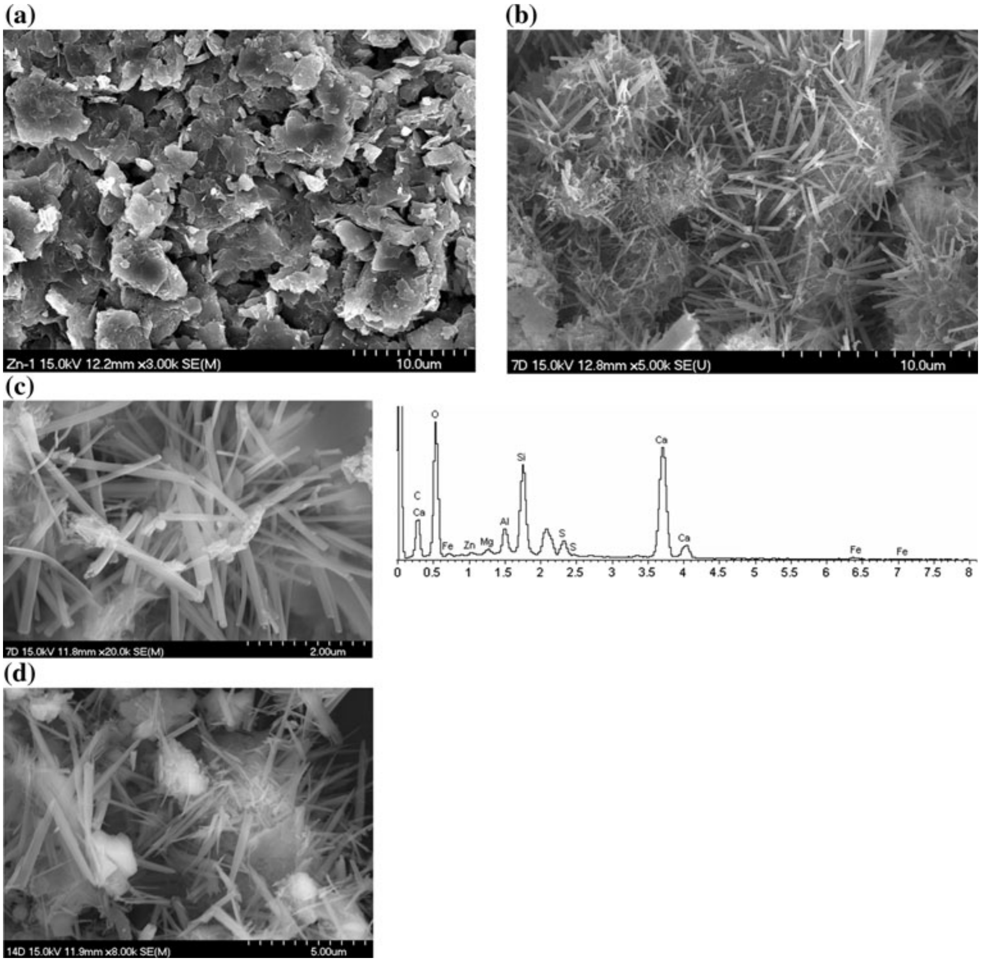

Fig. 6 SEM micrographs of the control and select treatments at 28 days: **a** control (×3,000); **b** 30 wt% PC (×5,000); **c** 30 wt% PC with EDX analysis (×20,000); and **d** 30 wt% CKD (×8,000)

of ettringite which from the prior XRPD analyses. The EDX results (Fig. 6c) of the 30 wt% PC treatment confirmed the ettringite was Zn-substituted with impurities of C, Si, Fe and Mg. However, $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, which has a platy morphology, was not observed in any SEM–EDX images.

Conclusions

In this study the Zn-contaminated soils from the Republic of Korea were stabilized using PC, CKD and FA. The effectiveness of the treatment was evaluated by the TCLP tests and the Universal Treatment Standard (UTS) of 4.3 mg/L. The TCLP results showed that 10 wt% PC and 15 wt% CKD treatments were successful in reducing the TCLP-Zn concentrations below the UTS limit of 4.3 mg/L after 7 days of curing. No significant reductions in the TCLP-Zn concentrations upon Class C FA treatment were observed. However, treatment combination of PC-Class C FA was effective in reducing the TCLP-Zn concentrations. XRPD results for PC and CKD treatments showed that Zn-substituted ettringite and $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ were possible phases responsible for Zn immobilization, but the latter phase could not be confirmed by SEM–EDX. Overall, the S/S treatment results indicated that CKD and PC-FA blends can be used cost effective alternatives for S/S when treating Zn-contaminated soils.

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