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Immobilization of Heavy Metals in Waste Phosphate Coating Sludge Using Kiln Dust as Portland Cement Substitute

G. Eker, V. Pinarli*

Department of Environmental Engineering, Uludag University, Turkey

Abstract In the present study, stabilization and solidification (S/S) of the waste phosphate sludge (WPS) using Portland cement (PC) and cement kiln dust (CKD) was investigated. In the first place, only PC was used to stabilize 5, 10 and 15% WPS. At a later stage, 10 and 15% CKD were used as PC substitute to stabilize 15%WPS. WPS contained initially 130.2 mg/L Zn and 22.6 mg/L Ni. U.S. Environmental Protection Agency (US-EPA) landfilling limits for Zn and Ni are 4.3 mg/L and 11 mg/L, respectively. Setting times and unconfined compressive strength (UCS) values were measured and permeability of selected samples was determined. TCLP (Toxicity Characteristics Leaching Procedure) and SPLP (Synthetic Precipitation Leaching Procedure) were applied to determine the concentrations of Zn and Ni leached from the mortar samples and leachate pH values were measured. Use of the CKD as a cement substitute delayed setting times, decreased UCS and increased leached heavy metal concentrations. Leached Zn and Ni concentrations of the WPS stabilized with PC and CKD following SPLP were lower than the EPA landfilling limits. However, leached Zn concentrations following TCLP were not compatible with the EPA limit. Leached Ni concentrations remained lower than the EPA limit. It was concluded that relatively low levels of alkalies, CaO and SiO_2 content of CKD negatively affected the setting, compressive strength and leaching characteristics.

Keywords Immobilization, Heavy Metals, Cement Kiln Dust

1. Introduction

Hazardous wastes are generally disposed in landfill after reduction of their toxicity [1]. Stabilization and solidification (S/S) process is one of the most common technologies to treat hazardous wastes before landfilling [2]. Portland cement (PC) is widely used as a binding agent for S/S application to reduce toxic characteristics of waste. Alkalinity of the PC make it suitable to fix heavy metals in the form of hydroxides, silicates etc. compounds which are less soluble forms of the heavy metals [3-5]. S/S process allow the using several pozzolanic materials such as cement kiln dust (CKD), fly ash, blast furnace slag, silica fume etc. as a cement substitute [2,6,7]. CKD is a by-product obtained from cement factories and thousands tons of it are disposed annually by cement companies [8].

Several researchers focused on the effect of the CKD to the cement hydration properties and S/S process [9-12]. Harthy *et al.* investigated the effect of 5-30% CKD substitution to strength development. It was noted that UCS results decreased with CKD replacement [11]. Alem *et al.* researched the role of CKD substitution in setting process of the cement and results showed that setting times decreased with using of CKD [10]. Furthermore, CKD can positively affect the hydration process and heavy metal fixation depends upon the chemical characteristics. It was reported that UCS results of the waste stabilized with PC and CKD were higher than the results of waste dust stabilized with only PC [12]. Leaching results of heavy metals such as Cd, Cr and Pb leaching results also showed that CKD was successful in reducing waste toxicity.

Effectiveness of the PC and CKD in S/S application are evaluated with the setting times, permeability, UCS and leaching tests etc. [2]. Setting time represents the beginning of the hardening process of the cement [2,13]. Measurement of the UCS shows the ability of the stabilized wastes to withstand overburden loads [14]. Permeability refers to the resistance of the material to the passage of water [15]. Leaching characteristics of the stabilized wastes are assessed by Toxicity Characteristics Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) which are proposed by USEPA for hazardous waste. TCLP and SPLP simulate landfilling condition and acid rain, respectively. Waste stabilized and solidified with binder can be determined as hazardous or non-hazardous according to concentrations of leached heavy metals [16-18].

Bursa is one of the large industrial cities in Turkey and automobile manufacturing is a major sector in the city. Waste phosphate sludge (WPS) is a residue from the phosphate coating process in automobile manufacturing industry. It is determined as a hazardous waste according to European Waste Catalog [19]. In one of the previous studies phosphate coating sludge was solidified using calcium aluminate cement [20]. It was noted that leaching results of the 15% WPS stabilized using only PC were higher than the EPA landfilling limits [21]. The aim of the present study was to investigate the effectiveness of the CKD as Portland cement substitute to reduce the toxic heavy metal concentrations of the S/S product containing 15% WPS. Evaluation was made according to leaching results compared to EPA landfilling limits [18]. Additionally, the influence of CKD substitution on the setting times and UCS of the samples were reported and discussed.

2. Experimental Work

Raw WPS was received from an automobile industry. WPS is produced during phosphate coating process which prevents corrosion of metal surface. WPS was dried in an oven at 105^{o}C for 24 hours before use. Ordinary PC was used as a main binder and CKD was used as a PC subsititute. The materials were obtained from the cement factory of Bursa. Moisture of the WPS was measured with Ohaus-MB200 machine. Specific surface areas of the WPS, PC, and CKD were measured by the Blaine apparatus Tonic Technic 72071. The pH values were measured using a HACH 54650 - 18 Sension 156 pH Meter. Specific gravity of the WPS, PC and CKD were measured by Multi Pycnometer-Quantachrome VP/11497101401. Chemical composition of the WPS was determined with X-Ray Spectrophotometer XEPOS/76004814 and composition of PC and CKD were determined with X-Ray Spectrophotometer ARL 8660. Chemical composition and physical properties of Portland cement, cement kiln dust and waste phosphate sludge were given in Table 1.

Paste and mortar samples were prepared. Water-to-solid ratio was chosen as 0.5. Rilem Cembureau Standard Sand was used in the mortar samples according to ASTM C 778-87. Setting times of the pastes were determined using Vicat needle apparatus. After being removed from their molds, the mortar samples were cured by immersion in water. Mortar samples cast in square prismatic mortar molds with internal dimensions of (40x40x160) mm. UCS values were determined using an ESEL ESL.25.001.B-015 250 kN compression machine after curing periods of 3, 7, 28, 56, and 90 days. Stress controlled loading speed setting of 0.05 kN/sec was applied for compression testing. Permeability of WPS solidified with PC was determined according to falling-head permeability method after 28 days of cure. The mortar samples were subjected to Toxicity Characteristics Leaching Procedure (TCLP) using an extraction fluid with pH 2.8 at end of the 28 days. Synthetic Precipitation Leaching Procedure (SPLP) intended to simulate precipitation was also applied using an extraction fluid with pH 4.2. Leachate pH values were measured following TCLP and SPLP extractions. Leached Zn and Ni concentrations were measured using Bausch & Lomb ARL/3520 AES Inductively Coupled Plasma (ICP).

Table 1. Chemical composition and physical properties of Portland cement, cement kiln dust and waste phosphate sludge

	PC	CKD	WPS
CaO (%)	65.41	43.60	0.02
SiO_2 (%)	20.43	12.52	0.18
Al_2O_3 (%)	5.71	4.16	0.59
Fe_2O_3 (%)	3.45	2.53	22.98
MgO (%)	0.77	0.54	0.11
P_2O_5 (%)	0.12	0.071	31.70
SO_3 (%)	2.43	0.34	0.01
Na_2O (%)	0.42	0.34	0.79
K_2O (%)	0.45	0.27	0.11
Cl^- (%)	0.01	0.01	0.03
LOI (%)	1.35	34.2	3.76
ZnO (%)	-	-	11.17
NiO (%)	-	-	0.58
Moisture (%)	-	-	75
pH	13	11	3.8
Specific gravity(g/m^3)	2.6	2.7	2.6
Specific surface area (cm^2/g)	3416	4222	3406

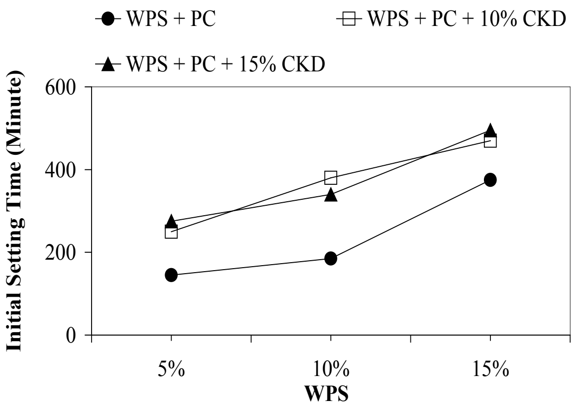
3. Results and Discussion

WPS was identified as hazardous waste in the European Waste Catalogue, with the code number of 110108 because of the high Zn and Ni concentrations. WPS contained 75% moisture as due to the wet conditions of phosphate coating bath. Heavy metal content of the WPS was measured as 130.2 mg/L Zn and 22.6 mg/L Ni. To be disposed safely in landfills according to the USEPA, Zn and Ni concentrations of the sludge should be lower than 4.3 mg/L and 11 mg/L, respectively [18]. Chemical composition and physical properties of the PC, CKD and WPS were determined. Major constituents of the PC and CKD were CaO, SiO_2, Al_2O_3 and Fe_2O_3. Alkali content of PC was higher than the CKD's. Furthermore, CKD has a relatively low Na_2O, K_2O and SO_3 content compared to the literature values up to 1.0%, 5.9%, 16.7%, respectively [22]. Specific gravity of the PC, CKD and WPS were similar, pH of the

PC and CKD were higher than pH of the WPS.

3.1. Setting Times of the Paste Samples Containing WPS, PC and CKD

Setting times were shown in Figure 1. Initial and final setting times increased with increasing WPS content. The results were longer than the setting times of the PC (as reference sample without WPS) measured as 80 minutes (initial) and 165 minutes (final). It was attributed to the retardation effect of Zn (9.0%) and P_2O_5 (31.7%) content of WPS [2,5,23].



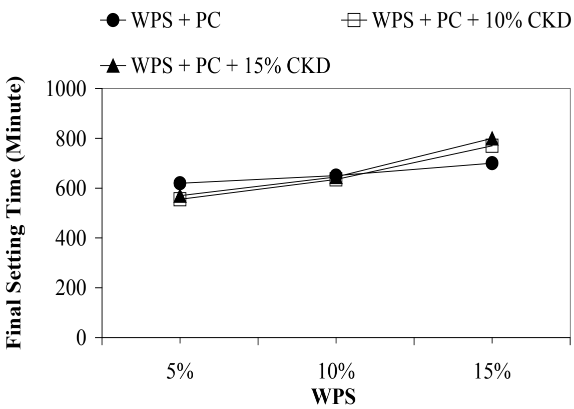


Figure 1. Setting times of the pastes containing waste phosphate sludge (WPS), Portland cement (PC) and cement kiln dust (CKD)

Initial setting times of paste samples were increased with using of CKD as cement substitute. Cement particles may have been coated by not only WPS but also by CKD at the beginning of the setting process. As a result, initial reactions between cement particles and water retarded. Formation of the first hydration products and then breaking of the layer delayed. Final setting time results of the paste sample containing 5% WPS was slightly decreased with CKD substitution. High specific surface area of the CKD may have contributed to acceleration of setting process by means of increased interaction with water [2]. Furthermore, it was thought that 5% WPS did not inhibite pozzolanic reactions. Final setting delayed with the using CKD to stabilize increased amount of WPS. CKD contained 0.2% K_2O and 0.3% Na_2O by weight. The alkali content of the CKD was much lower than that of reported in the literature [2,12]. Retardation of setting process was attributed to low alkali content of the CKD. It is known that alkali (Na_2O and K_2O) salts contribute to the raise in pH, inhibit the formation of $CaSO_4$ and as a result, accelerate setting process [10,24,25].

3.2. Unconfined Compressive Strength Results of the Mortar

UCS values at the end of the 3, 7, 28, 56 and 90 curing days are shown in Figure 2. UCS results of the mortar samples containing 15% WPS and 85% PC were lower than the results of the reference sample. Phosphate and zinc precipitates which coat the surface of cement grains as a layer might have formed, thus preventing the hardening process [21,26,27].

UCS values of the WPS stabilized with PC and 10% CKD as a cement substitute were not lower than the results of WPS stabilized with only PC. However, UCS results were decreased with increasing amount of the CKD substitution from 10% to 15%. Retardation of setting can affect the UCS results during the early curing ages [27]. Decreases in UCS results were attributed to lower CaO (43.60%) and SiO_2 (12.5%) content of the CKD than content of PC (CaO: 65.4, SiO_2: 20.4). It is known that these components constitute C_3S which is one of the important phases responsible for strength development after set [2].

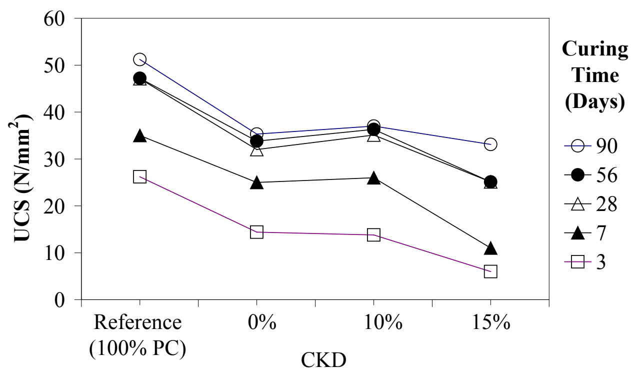


Figure 2. Unconfined compressive strength (UCS) values of the mortar samples

3.3. Relationship between Unconfined Compressive Strength and Permeability

Permeability was increased while UCS was decreased with increasing of the WPS ratios as shown in Figure 3. Results indicated that there was an adverse relation between UCS and permeability. 5% WPS stabilized with PC was defined as non-permeable material (permeability<10^{-8} cm/sec) and other samples containing 10-15% WPS were defined as a semi-permeable materials. EPA requires permeability values less than 10^{-7} cm/sec to safely dispose in landfill [28]. Result of 5% WPS stabilized with PC was in accordance with EPA value.

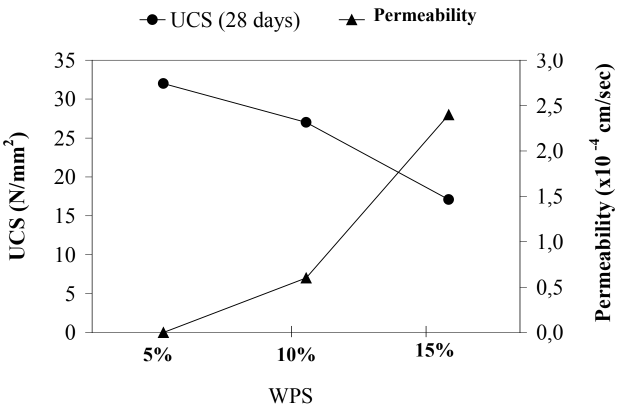


Figure 3. Relationship between unconfined compressive strength (UCS) and permeability of waste phosphate sludge (WPS) solidified with Portland cement

3.4. Leaching Results of Mortar Samples

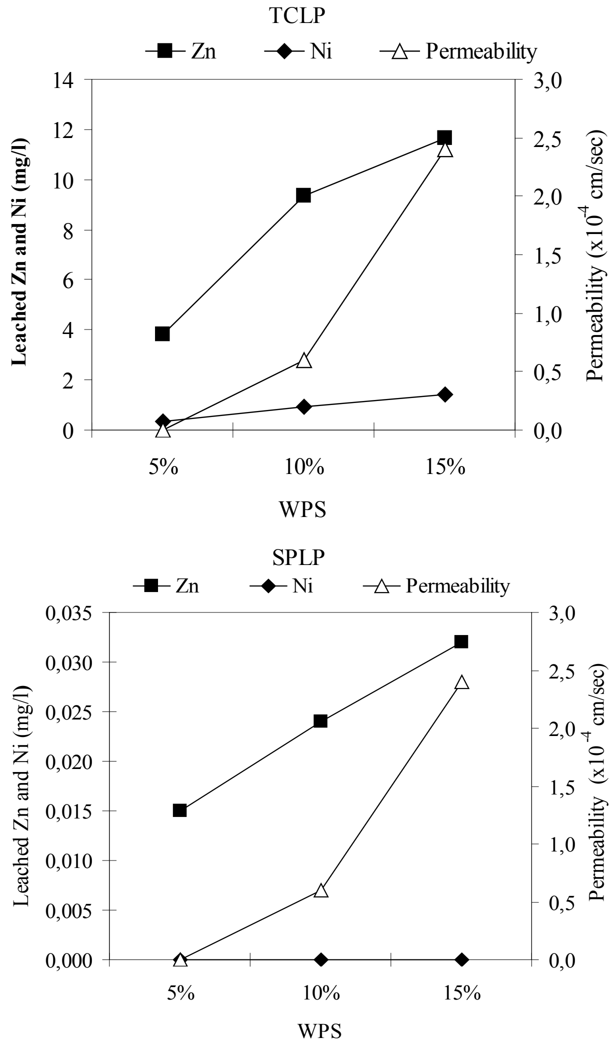


Figure 4. Relationship between heavy metal leaching following leaching and permeability of waste phosphate sludge (WPS) solidified with Portland cement a) TCLP b) SPLP

Relationship between leaching and permeability: Relation between leached heavy metal concentrations and permeability results of the WPS stabilized with only PC are shown in Figure 4a (TCLP) and Figure 4b (SPLP). Following TCLP and SPLP extractions, leaching of Zn and Ni increased with increasing of the permeability. It was showed that permeability of the S/S product was an important factor, as it indicated transport of contaminants from stabilized waste to the environment.

Role of CKD in heavy metal fixation: Fixation of Zn and Ni decreased with using of CKD as a cement substitute. 91% Zn and 94% Ni were fixed in 15% WPS stabilized with only PC. Fixation ratios were decreased to 87% Zn and 91% Ni with 15% CKD used as PC substitute. Leached heavy metal concentrations increased with increasing amount of CKD (Figure 5). Leached Zn concentrations remained above the EPA landfilling limit. However, Ni concentration conformed to the EPA limit. Inefficiency of the CKD was due to its lower CaO, SiO_2 and alkali content comparing with PC. Relatively low amount of alkali components reduce formation of hydrate products which support high specific surface area to fixation of heavy metals. Furthermore, low amount of CaO and SiO_2 in the mixture mean that less amount of C_3S phase is formed which is required for Zn fixation [12,29]. In the present study, decrease in the amount of these constituents probably reduced the amounts of the hydration products, WPS also might be interacted with PC-CKD reactions.

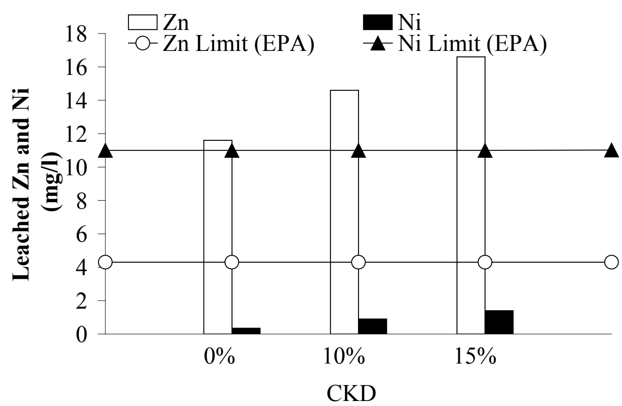


Figure 5. Zinc and nickel leached from the 15% waste phosphate sludge solidified with Portland cement and cement kiln dust (TCLP)

TCLP and SPLP results: Leached heavy metal concentration increased as the pH values decreased. It was seen that the leachabilities of the metals were pH dependent. Leachate pH following TCLP decreased from 5.2 to 4.8 when CKD used as cement substitute and the solubility of Zn and Ni increased. Low pH values were attributed to the relatively low alkali content of CKD. Results indicated that PC substitution by CKD reduced the alkaline nature of the system. Zn concentrations leached from S/S products after SPLP extraction were not higher than 0.2 mg/L. This value conformed with the EPA landfilling limit.

4. Conclusions

The following conclusions may be drawn from this study:

- Setting time prolonged as CKD ratios in the sample increased. Possible reason of retardation was relatively low alkali content of the CKD.
- Permeability of the mortar samples increased as the UCS decreased. It was found that the more permeable stabilized products had lower UCS. Also, leached Zn and Ni increased with permeability.
- UCS results were decreased with increasing CKD substitution ratio from 10% to 15%. Lower CaO and SiO_2 content of the CKD with respect to PC negatively affected the strength development.
- Leached Zn and Ni concentrations increased with CKD substitution.
- TCLP results showed that the leached Ni concentrations were lower than the EPA landfilling limits. However, the leached Zn concentrations were higher.
- Leached Zn and Ni concentrations following SPLP extraction were lower than the EPA limits.

Relatively low levels of alkalies, CaO and SiO_2 content of CKD negatively affected the setting, hardening and leaching processes. It can be concluded from the results of the present study that the required degree of stabilization of 15% WPS using CKD as a PC substitute was not achieved. Using other pozzolanic materials for WPS stabilization may be investigated in further studies.

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