

Stabilization/solidification of lead-contaminated soil using cement and rice husk ash

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Abstract

This paper presents the findings of a study on solidification/stabilization (S/S) of lead-contaminated soil using ordinary Portland cement (OPC) and rice husk ash (RHA). The effects of varying lead concentrations (in the form of nitrates) in soil samples on the physical properties of their stabilized forms, namely unconfined compressive strength (UCS), setting times of early mixtures and changes in crystalline phases as well as chemical properties such as leachability of lead, pH and alkalinity of leachates are studied. Results have indicated that usage of OPC with RHA as an overall binder system for S/S of lead-contaminated soils is more favorable in reducing the leachability of lead from the treated samples than a binder system with standalone OPC. On the other hand, partial replacement of OPC with RHA in the binder system has reduced the UCS of solidified samples.

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1. Introduction

Lead-based contaminants have always been major sources of contamination to the environment during these past decades due to thriving global industrialization. Anthropogenic activities such as agriculture and manufacturing of industrial goods have directly or indirectly contributed mass amounts of lead-based contaminants into the environment, of which soil surface and subsurface are among the recipients. It is an established fact that these soil contaminants present serious environmental and health hazards, particularly to young children of which lead poisoning is prevalent [1]. The soil remediation technique of solidification/stabilization (S/S) offers an effective means of treating the lead-contaminated soils by significantly reducing the mobility and solubility of lead in the soils. Recent research on S/S of metal-contaminated soils was focused primarily on standalone ordinary Portland cement (OPC) systems or incorpo-

ration of other established pozzolans such as pulverized fly ash (PFA) and lime. While these S/S systems exhibit excellent treatment effectiveness, their applications in Asian countries have drawbacks which include relatively high costs of cement and lime as well as limited availability of mass amount of fly ashes. Concurrently, these countries are experiencing predicament in disposal of rice husk heaps due to their abundance. Concrete technologists are gradually finding applications in rice husk ash (RHA) as an additive for producing high-strength concrete but there is no identified usage of RHA in S/S of contaminated soils. The use of rice husk ash, an indigenous agro-waste in its raw form, as a supplementary binder to cement for treatment of contaminated soils not only marks a novelty in the S/S technology but also assists in alleviating disposal problem of rice husk heaps in Asian countries. The objective of this study was to investigate the effects of varying lead concentrations (in the form of nitrates) in soil samples on the physical properties of their stabilized forms (due to S/S by OPC and RHA), namely unconfined compressive strength (UCS), setting times of early mixtures and changes in crystalline phases as well as chemical properties such as leachability of lead, pH and alkalinity of leachates.

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2. Materials and methods

2.1. Collection and spiking of soil

Control soil was collected within University of Malaya campus near the Reserve Officer Training Unit (ROTU) complex. The soil was screened on-site by using a 2-mm sieve prior to collection. The soil was then oven-dried at 105 °C overnight to remove moisture and repress microbial activity. The soil was spiked by mixing known quantity of reagent grade lead(II) nitrate (0, 500 and 25,000 mg/kg) provided by Merck. The nitrate form of lead was chosen due to its high solubility (high potential for high cation mobility) and the fact that it does not inhibit solidification/stabilization reactions [2]. Spiked soils were prepared by mixing predetermined amount of lead(II) nitrate with ASTM type II deionized water prior to addition into the control soil. The soil was mixed thoroughly to ensure homogeneous distribution of the contaminant in the soil.

2.2. Binder systems

Treatment of the lead-spiked soil was conducted using Type I OPC as the main binder and supplemented by RHA. The OPC was obtained from Associated Pan Malaysian Cement while raw rice husk was obtained from a BERNAS rice mill at Kuala Selangor, Malaysia. A simple ferrocement incinerator was used for burning the rice husk under controlled conditions. Burning of rice husk was initiated by providing the burning source at the bottom of the incinerator for 1 h and was left for 2 days (burning was self-sustained) prior to collection of burnt rice husk. The burnt rice husk was then ground with Los Angeles machine for 5000 cycles to produce ash.

2.3. Production of solidified/stabilized samples

The binder (OPC with or without RHA) was added to either the control or spiked soil at cement-to-dry soil (C/S_d) ratios of 0.5, 1.0 and 2.0. Mixing of these materials was conducted in a 25-L SPAR type mixer. The soils were homogenized for 15 min prior to the addition of ASTM type II deionized water. It was ensured that the addition of water to the binder and soil was adequate to produce a mixture with a flow of 10% by using a K-slump tester specified in ASTM 1362-97 [3]. The mixture was cast into 50 mm × 50 mm × 50 mm steel cube molds and 1-L high-density polyethylene (HDPE) in three layers, with each layer compacted by means of a vibrating table to yield good packing of the mixture. Solidified cubic samples for unconfined compressive strength determination were prepared in triplicates. After the initial mixing, 1 day was allowed for setting before the solidified samples were demolded. A further 55 days were allowed for air drying of the solidified samples in a cabinet at a controlled condition (temperature = 25 ± 2 °C, humidity > 80%). Table 1 summarizes the mix design for the study.

2.4. Testing protocols

The testing protocols in this study included: (a) setting time, (b) UCS, (c) pH and alkalinities of TCLP/SPLP leachates, (d)

Table 1
Mix design

Concentration of lead(II) nitrate (mg/kg)	C/S_d	Percentage of OPC in binder (%)	Percentage of RHA in binder (%)
0 (control)	0.5	100	–
	1	100	–
	2	100	–
500	0.5	100	–
	1	100	–
	2	100	–
25000	0.5	100	–
	1	100	–
	2	100	–
	1	90	10
	1	80	20
	1	70	30

leachability of lead using the Toxicity Characteristics Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) tests and (e) changes in crystalline phases using X-ray diffractometry (XRD). The initial and final setting times of the mixtures were determined by using the modified method of BS 4550: Part 3, Section 3.6. Equivalent portions (by weight) of binder and spiked soil were mixed to give a C/S_d ratio of 1 as opposed to only the binder as stipulated by the standard method. The concentrations of lead(II) nitrate in soil are listed in Table 2. Mixing of the binder and soil was carried out in a SPAR type mixer for 15 min to ensure homogeneity. ASTM type II deionized water was added to produce a mixture with a flow of 10% by using the K-slump tester. It was considered appropriate to proceed in this manner rather than mixes of similar consistency in order to obtain indications vis-à-vis the capability of lead(II) nitrate to accelerate or retard the mixture setting times at the same workability. Apart from the modified steps, all other aspects of the method remained the same.

The solidified cubic samples were subjected to the UCS test in accordance with BS 1881: Part 116: 1983 [4] after 1, 3, 7, 14, 28 and 56 days of air drying. Crushed block leaching tests, namely TCLP [5] and SPLP [6] were conducted on the treated samples subsequent to 28 days of air drying. The leaching solutions used

Table 2
Concentrations of lead(II) nitrate in soil for determination of setting times

Concentration of lead(II) nitrate (mg/kg)	Percentage of OPC in binder (%)	Percentage of RHA in binder (%)
0 (control)	100	–
500	100	–
5000	100	–
25000	100	–
50000	100	–
25000	90	10
25000	80	20
25000	70	30

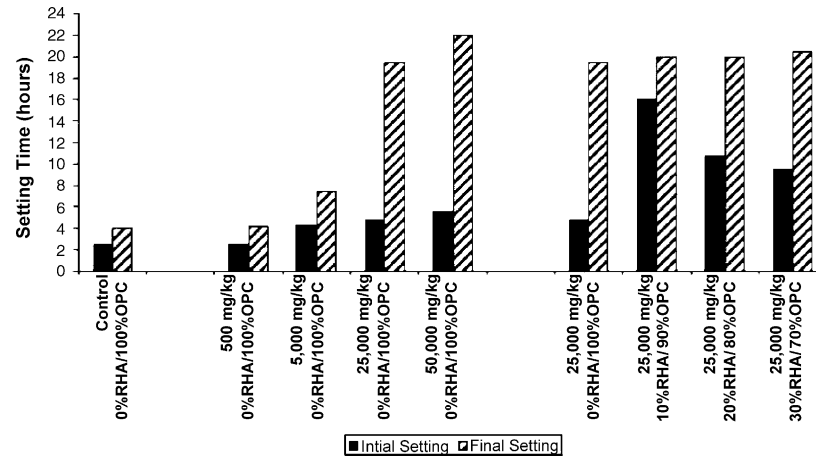


Fig. 1. Comparison of initial and final setting times of stabilized soils for C/S_d ratio of 1.

in the TCLP test were acetic acid (pH 2.88) and deionized water (pH 6.80) while a mixture of dilute nitric and sulfuric acids (pH 6.80) was used in the SPLP test. Subsequent to completion of the 18-h extraction, pH and alkalinity [7] tests were conducted on both the unfiltered and filtered leachates. The changes in crystalline phases of the stabilized soils subsequent to 28 days of air drying for C/S_d ratio of 1 were determined by means of XRD. The samples were manually ground to fine powders in a pestle and mortar prior to XRD analysis using the PHILLIPS X'Pert MPD 3040 powder diffractometer for the reflection angle (2θ) in the range $5\text{--}90^\circ$. Crystalline phases and peaks were identified by using the Joint Committee on Powder Diffraction Standards (JCPDS) database.

3. Results and discussion

3.1. Setting times

Setting time of a cementitious mixture is referred to as the period when water is introduced into the mixture system to the onset of hardening. The initial set time occurred when the Vicat needle 1.13 mm in diameter penetrated the mortar mixture to a point 5 ± 1 mm from the bottom of the mold. Final setting time is defined as that at which the 5-mm cap ring left no noticeable mark when placed on the surface of the mortar mixture. Fig. 1 shows the comparison of initial and final setting times of stabilized soils for C/S_d ratio of 1. The result indicated that the final setting times were directly correlated with their corresponding initial setting times in which the former exhibited similar setting trend shown by the latter. An increase in initial setting time of the mixture also caused increase in final setting time of the same mixture. Significantly lengthened final setting times (>19 h) were recorded for 25,000 and 50,000 mg/kg lead(II) nitrate as well as all the RHA-incorporated mixtures of the same contaminant. Increases of these setting times caused by the presence of these contaminants in this study confirmed the notion that materials that cause the retardation of set often bring about increased long-term strength in Portland cement systems [8].

3.2. Stabilized/solidified waste acceptance criteria

Table 3 lists the stabilized/solidified waste acceptance criteria which were used to evaluate the effectiveness of the treatment. These criteria were compiled due to the non-existence of soil and groundwater standards as well as stabilized/solidified waste treatability criteria in Malaysia. The two characteristics selected for assessment of the treated soils were UCS and leachability since the two were the predominant criteria assessed for the effectiveness of solidification/stabilization treatment in the United States [9]. The regulatory UCS and leachability limits were extracted from two sources; regulatory waste disposal limit at a disposal site in the United Kingdom [10] and the maximum concentration of contaminants for toxicity characteristic of solid wastes from US Environmental Protection Agency [5].

3.3. UCS of stabilized/solidified samples

It was observed that UCS values of all the solidified samples exceeded the minimum mortar limit of 20 N/mm^2 . From Fig. 2, the addition of 500 mg lead(II) nitrate per kg of soil exhibited an indistinct effect on the UCS of solidified samples where the UCS of the control sample at 56 curing days was lower than the 500 mg/kg lead(II) nitrate sample at C/S_d ratio of 0.5 and conversely true for similar samples at C/S_d ratio of

Table 3
Stabilized/solidified waste acceptance criteria

Characteristic	Regulatory (acceptance) level
Compressive strength at 28 days (N/mm^2)	Landfill disposal limit ^a : 0.34 Comparative mortar limit ^a : 20
Leachability (mg/L)	Cadmium ^b : 1.0 Chromium ^b : 5.0 Lead ^b : 5.0 Copper ^a : 5.0 Zinc ^a : 10.0

^a Regulatory waste disposal limit at a disposal site in the UK [10].

^b USEPA maximum concentration of contaminants for toxicity characteristic [5].

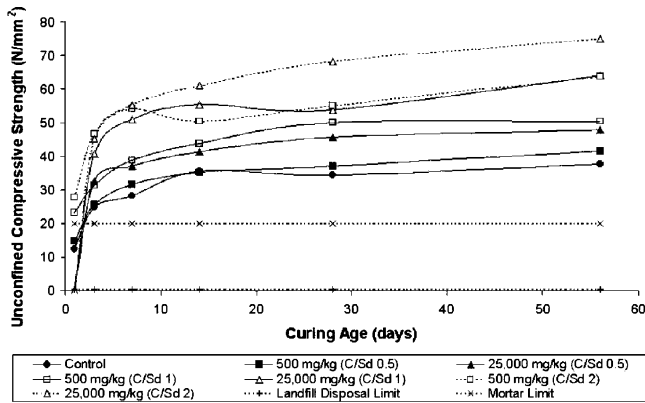


Fig. 2. UCS development of stabilized/solidified lead(II) nitrate-spiked soils (100% OPC).

1 and 2. However, the UCS values of solidified 25,000 mg/kg lead(II) nitrate samples were higher than both the control as well as 500 mg/kg lead(II) nitrate samples at all the C/S_d ratios. Fig. 3 evidently shows the effect of replacement of OPC with RHA on the UCS development of solidified spiked soils for C/S_d of 1. Replacement of OPC with RHA unambiguously reduced the UCS of solidified lead-spiked samples. For the solidified 25,000 mg/kg lead(II) nitrate samples, replacements of 10, 20 and 30% OPC with RHA constituted UCS decreases of 14.6, 9.9 and 6.7 N/mm² from preceding percentages, respectively, at 56 days of curing.

3.4. pH and alkalinities of leachates

The pH values of all leachates were essentially alkaline ranging from 11.92 to 12.78 (TCLP—deionized water), 10.04 to 11.98 (TCLP—acetic acid) and 12.08 to 12.76 (SPLP—nitric/sulfuric acid). It was also observed that pH values of deionized water and sulfuric/nitric acid leachates were primarily within the range of 12–13 while the pH values of acetic acid leachates were predominantly within the relatively lower range of 11–12. For crushed block leachates with the C/S_d ratio of 1, the incremental replacement of OPC with RHA reduced the pH of the acetic acid leachates from 11.84 to 10.53 corresponding to the RHA incremental percentages

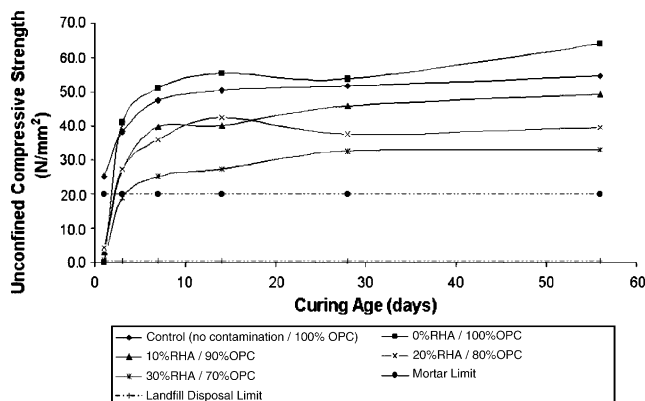


Fig. 3. Effect of replacement of OPC with RHA on the UCS development of stabilized/solidified 25,000 mg/kg lead(II) nitrate-spiked soils for C/S_d of 1.

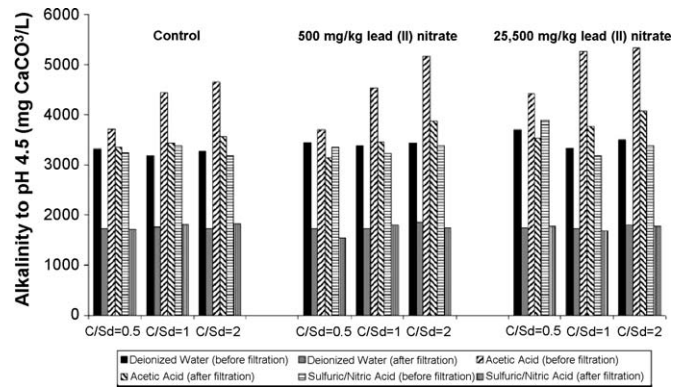


Fig. 4. Alkalinities of leachates to pH 4.5 for control and lead(II) nitrate samples (100% OPC).

from 0 to 30% while pH of the other two leachates remained constant.

Fig. 4 shows the alkalinities of leachates to pH 4.5 for control and lead-spiked samples which were treated with 100% OPC. Alkalinity was reported as “mg CaCO₃/L” in order to indicate that the measured sample had alkalinity equivalent to that of a solution with a certain dissolved amount of calcium carbonate (CaCO₃). It was observed that alkalinities of both unfiltered and filtered leachates were very high (in the range of 5329–662 mg CaCO₃/L) as compared to the alkalinity range of typical earth surface water (10–150 mg CaCO₃/L). The effect of presence of crushed solidified samples in the leachates on their alkalinity was evident as there were significant differences in measured alkalinity prior and subsequent to filtration. For both deionized water and sulfuric/nitric acid leachates, the reduction of all measured alkalinities subsequent to filtration averaged 50% while alkalinity reduction for acetic acid leachates averaged 20%. The authors postulated that these substantial differences of measured alkalinities between the unfiltered and filtered leachates were attributed to the presence of unreacted Ca(OH)₂ (in which its presence was confirmed in the XRD analysis elucidated in Section 3.6) in the crushed blocks of the unfiltered leachates prior to titration that provided additional acid buffering capacity to the system. A more comprehensive elucidation was that addition of acid into the unfiltered leachates prompted leaching of more hydroxide ions from the crushed blocks into the solution system (which was already heavily populated with OH⁻ ions) and thus increased the amount of acid required to reduce the pH to 4.5. This did not occur in the filtered leachates as the amount of hydroxide ions remained constant throughout titration. Another notable observation was that the alkalinities of the both unfiltered and filtered acetic acid leachates were substantially higher than that of deionized water and sulfuric/nitric acid leachates. This may be due to the relatively higher acidic concentration and pH of the acetic acid (0.1 M; pH 2.88) when used as a crushed block leaching solution which promoted leaching of more OH⁻ ions from the crushed blocks as compared to weaker acidic concentrations of the deionized water (pH 6.8) and sulfuric/nitric acid (<0.05 M; pH 4.2) solutions. From Fig. 4, the effect of C/S_d ratio increments on the alkalinity of the leachates was more apparent for the acetic acid leachates where increases

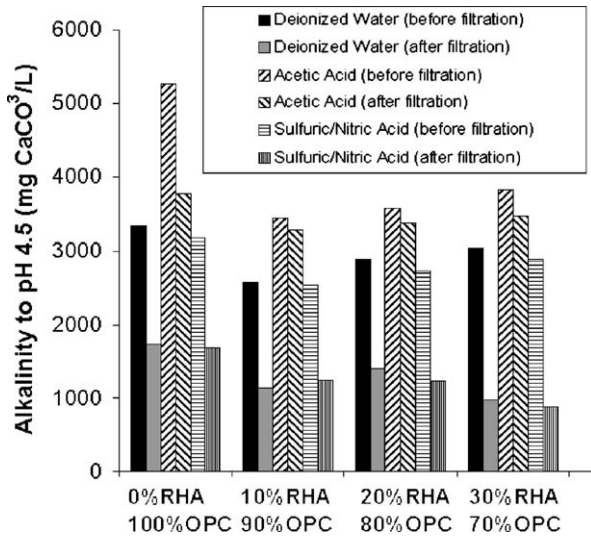


Fig. 5. Effect of replacement of OPC with RHA on the alkalinities of crushed block leachates for C/S_d of 1 (25,000 mg/kg lead(II) nitrate).

of the C/S_d ratios from 0.5 to 2.0 increased their alkalinities. Conversely, this effect was less distinctive for the other two leachates as there were marginal alkalinity fluctuations instead of a discernible trend for the similar C/S_d increments.

RHA is predominantly consisted of silicon dioxide (SiO_2) but appreciably devoid of alkaline-based constituents such as calcium and magnesium oxides [11] which are typical elements of OPC. It is, therefore, anticipated that incorporation of RHA into the binder system would reduce the alkalinities of the crushed block leachates. The effect of incorporating RHA into the binder system on the alkalinities of the crushed block leachates for C/S_d ratio of 1 is shown in Fig. 5. For the 25,000 mg/kg lead(II) nitrate leachates, their alkalinities were reduced with the OPC replacement with RHA from 0 to 10% but 10 to 20% and 20 to 30% replacements constituted an anomaly in the result where the alkalinities generally increased onwards.

3.5. Leachability

Fig. 6 shows the lead concentrations in the OPC-treated crushed block leachates. Overall, the leached lead concentrations in the three different leachates were either undetectable or appreciably below the proposed leachability criteria of 5 mg/L for the 500 mg/kg lead(II) nitrate. Only the lead concentrations in the 25,000 mg/kg lead(II) nitrate leachates (deionized water and sulfuric/nitric acid) at C/S_d ratio of 0.5 exceeded 5 mg/L. Increases of C/S_d ratios clearly reduced the leachability of lead from the crushed blocks. An atypical observation was that the acetic acid leachates contained low concentrations of leached lead as compared to both deionized water and sulfuric/nitric acid leachates.

Fig. 7 shows the effect of replacement of OPC with RHA on the leachability of lead for C/S_d ratio of 1. The result clearly indicated that leachability of lead from the crushed blocks was reduced due to incorporation of RHA into the binder system where the lead concentrations were reduced from 3.70 to

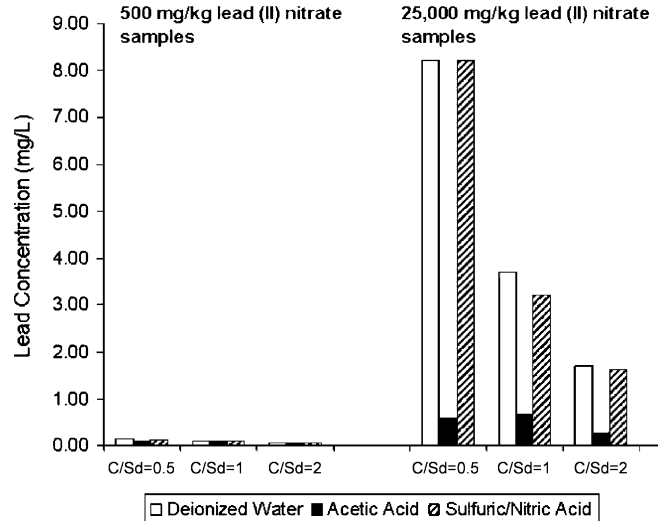


Fig. 6. Lead concentrations in crushed block leachates (100% OPC).

1.06 mg/L (deionized water), 0.66 to 0.08 mg/L (acetic acid) and 3.22 to 1.18 mg/L (sulfuric/nitric acid) corresponding to the RHA incremental percentages from 0 to 30%. This significant finding augurs well for usage of RHA in the field of S/S of metal-contaminated soil.

3.6. Changes in crystalline phases

The changes in crystalline phases of OPC as well as RHA stabilized soils were determined by means of XRD. XRD patterns reveal phase, chemical and crystalline structure information data which provide greater comprehension on the composition as well as reaction products of OPC/RHA stabilized contaminated soil prior and subsequent to chemical stabilization. Fig. 8 shows the XRD patterns of lead(II) nitrate contaminated soils prior and subsequent to S/S treatment at 28 curing days. The diffraction intensities which were reflected by corresponding counts per

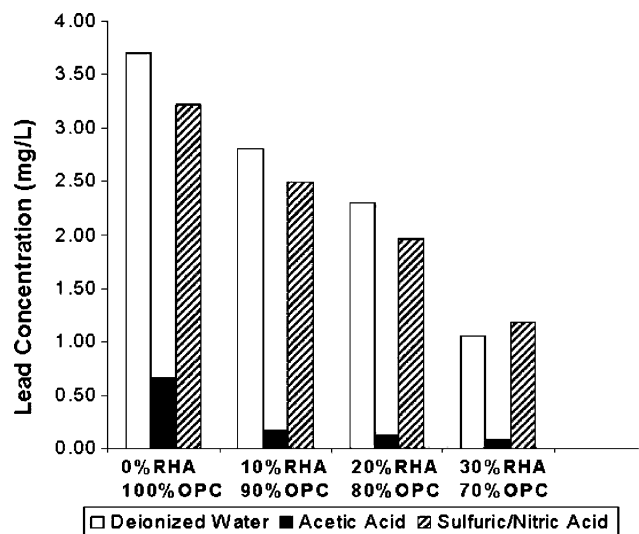


Fig. 7. Effect of replacement of OPC with RHA on the leachability of lead for C/S_d ratio of 1 (25,000 mg/kg lead(II) nitrate).

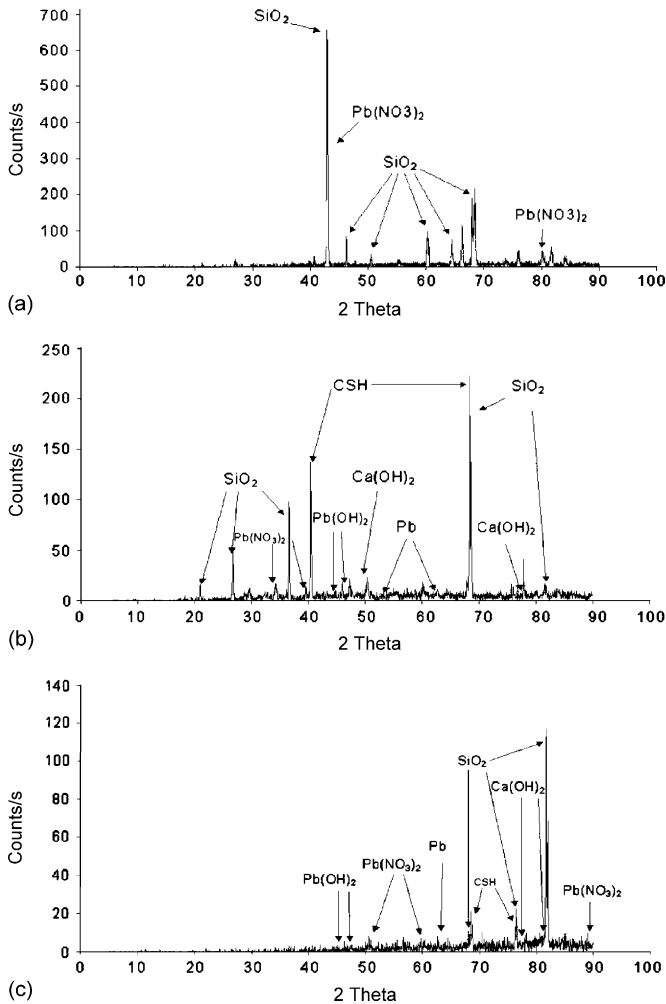


Fig. 8. XRD patterns of lead(II) nitrate spiked-soils prior and subsequent to S/S treatment at 28 curing days for the samples (a) untreated lead(II) nitrate soil; (b) 0%RHA/100%OPC + $\text{Pb}(\text{NO}_3)_2$ soil; (c) 30%RHA/70%OPC + $\text{Pb}(\text{NO}_3)_2$ soil.

second (cps) were utilized as the indication of changes among the patterns of various systems.

The most prominent peaks in the pattern of untreated contaminated soils were those of silicon dioxide (SiO_2) (quartz) at 2θ of 42.74° , 46.10° , 50.47° , 60.38° , 64.46° and 68.81° . Prior to treatment, there were discernible $\text{Pb}(\text{NO}_3)_2$ peaks at 2θ of 43.06° and 79.99° . Subsequent to treatment with OPC and RHA, decrease in intensities corresponding to $\text{Pb}(\text{NO}_3)_2$ peaks coupled with the presence of CSH as well as portlandite ($\text{Ca}(\text{OH})_2$) substantiated the occurrence of stabilizing cementitious reactions in both 0%RHA/100%OPC and 30%RHA/70%OPC-treated soils. $\text{Ca}(\text{OH})_2$ was a significant product of cement hydration in this study. The presence of lead hydroxide ($\text{Pb}(\text{OH})_2$) peaks at 2θ of 45.30° and 47.04° also indicated that lead in $\text{Pb}(\text{NO}_3)_2$ had precipitated to form $\text{Pb}(\text{OH})_2$ within the cement hydration environment which explained the high treatment efficiency due to low solubility of the precipitates. This observation supports the finding of a study conducted by Li et al. [12] which suggested that heavy metals such as lead could exist in the S/S matrix as metal hydrated phases or metal hydroxides precipitating on the surface of CSH. It was determined that some residual portlandite

was identified for all the treated contaminated soils. This indicated that pozzolanic reactions were not over by the end of the 28-curing day period.

4. Conclusions

Results indicated that usage of OPC with RHA as an overall binder system for S/S of lead-contaminated soils showed tremendous potential as evident in the regulatory compliance of two predominant post-treatment test parameters, namely UCS and leachability of metals. Incorporation of RHA in the binder system was justified as leachability of lead from the treated samples was reduced corresponding to incorporation of RHA increments from 0 to 30%. Even though partial replacement of OPC with RHA in the binder system reduced the UCS of solidified samples, it was still high enough to exceed the mortar limit of 20 N/mm^2 , which was more than sufficient to be reused as construction materials. The presence of lead(II) nitrate increased the initial and final setting times of mortar mixtures. Initial incorporation of 10 wt% RHA into the binder system significantly increased the mixture's initial setting time while subsequent RHA incorporations conversely reduced the mixture's initial setting times. Lead in nitrate form had precipitated to form lead hydroxide within the cement hydration which explained the high treatment efficiency due to low solubility of the precipitates. Pozzolanic reactions were not over by the end of the 28-curing day period as residual portlandite was identified for all the treated samples.

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