



# Article Stabilization/Solidification of Zinc- and Lead-Contaminated Soil Using Limestone Calcined Clay Cement (LC<sup>3</sup>): An Environmentally Friendly Alternative

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Abstract: Due to increased carbon emissions, the use of low-carbon and low-cost cementitious materials that are sustainable and effective are gaining considerable attention recently for the stabilization/solidification (S/S) of contaminated soils. The current study presents the laboratory investigation of low-carbon/cost cementitious material known as limestone-calcined clay cement (LC<sup>3</sup>) for the potential S/S of Zn- and Pb-contaminated soils. The S/S performance of the LC<sup>3</sup> binder on Znand Pb-contaminated soil was determined via pH, compressive strength, toxicity leaching, chemical speciation, and X-ray powder diffraction (XRPD) analyses. The results indicate that immobilization efficiency of Zn and Pb was solely dependent on the pH of the soil. In fact, with the increase in the pH values after 14 days, the compressive strength was increased to 2.5–3 times compared to untreated soil. The S/S efficiency was approximately 88% and 99%, with increase in the residual phases up to 67% and 58% for Zn and Pb, respectively, after 28 days of curing. The increase in the immobilization efficiency and strength was supported by the XRPD analysis in forming insoluble metals hydroxides such as zincwoodwardite, shannonite, portlandite, haturite, anorthite, ettringite (Aft), and calcite. Therefore, LC<sup>3</sup> was shown to offer green and sustainable remediation of Zn- and Pb-contaminated soils, while the treated soil can also be used as safe and environmentally friendly construction material.

**Keywords:** low carbon materials; heavy metal immobilization; sustainable remediation; environmentally friendly materials

# 1. Introduction

Soil contaminated with heavy metals is a serious threat to the sustainable development and global food security [1–4]. In contrast to water and air pollution, heavy metal pollution in soils is an invisible and unseen problem [1,5–9]. Many of the world's contaminated sites have become the dump sites of various industrial by-products that contain inorganic pollutants such as heavy metals. As these heavy metals come in contact with water, the human health and environment within the ecosystem become potentially at risk [10,11]. Among the hazardous heavy metals zinc (Zn) and lead (Pb) are considered as the harmful pollutants that exist at elevated levels in most of the contaminated sites around the world [12]. Further, Zn and Pb are not only harmful to human health and environment, but also

lead to mechanical-chemical degradation of contaminated soils, which in turn results in unfavorable conditions for the redevelopment of contaminated sites. It is therefore imperative to identify a time- and cost-effective remediation method for the treatment of heavy metal-contaminated soils, consequently the treated soils can be reused as safe and environmentally friendly construction materials.

Stabilization/solidification (S/S) is considered to be most appropriate method for immobilization of heavy metal-contaminated soils due to its ease and workability among the available effective remediation methods [13–16]. Besides, the United States Environmental Protection Agency (USEPA) recognizes S/S as the best demonstrated available technology (BDAT) for treating hazardous metals [7,17,18]. The mechanisms involved in S/S treatment is as follows: stabilization refers to reducing the hazard potential by converting contaminants into their least soluble/toxic form [19,20], whereas solidification is the encapsulation of waste in a monolith mass of high structural integrity that involves both mechanical binding and chemical interaction between solidifying agents such as cementitious materials, which further restricts the movement of heavy metals by isolating them into less/insoluble crystalline phases [14]. The performance of S/S depends on the nature of the contaminants (organic/inorganic) and binders used. Inorganic heavy metals are commonly immobilized via chemical reaction and physical encapsulation by forming barely insoluble metal hydroxides. Thus, the binder plays a key role in the S/S process, and the development of novel binders has gained special attention recently, specifically low carbon/cost binders. In a previous study, the authors revealed that partial replacement of calcined clay (CC) and limestone (LS) with ordinary Portland cement (OPC) has better immobilization efficiency for Zn-contaminated soils (Reddy et al. [21]). In addition, various hydration products, such as portlandite, ettringite, tri-calcium silicate, and wulfingite, were found to be responsible for the immobilization of Zn-contaminated soils. In addition, Wang et al. [6] reported that supplementary cementitious materials (SCMs) such as CC and LS have improved immobilization efficiency in treating both oxy-anionic As- and cationic Pb-contaminated soils. The leachability efficiency of CC and LS was approximately 96% and 99% for As and Pb, respectively. Further, addition of LS to CC promotes the transformation of metastable hydroxyl-rich Afm to stable carbonate rich Afm, which increases the degree of polymerization in calcined clay hydrates, resulting in enhancement of mechanical properties. Therefore, replacing SCMs with the conventional cement binders has a better performance in treating heavy metal-contaminated soils.

Recently, a new ternary blend known as limestone-calcined clay cement LC<sup>3</sup> was successfully demonstrated in the authors' previous study on Zn-contaminated soils [21]. LC<sup>3</sup> is known as a low-carbon and low-cost binder since the production process involves replacement of low grade calcined clays (CC) and limestone (LS). Typically, LC<sup>3</sup> is a ternary blend of 30% CC, 15% LS, and 5% gypsum replaced with 50% cement clinker. The replacement of low-grade limestone and low-grade kaolinitic clay with (kaolinite content > 40%) when calcined at 750 °C undergoes hydroxylation to form CC/metakaolin (MK) [6] as presented in Equation (1), which possess high pozzolanic reactivity due to the presence of alumina- and silicate-rich phases. Further, when LS reacts with CC it produces carboaluminosilicates-rich mineral phases that are responsible for the formation of primary and secondary hydration products such as calcium silicate hydrate (C-S-H), calcium hydrate (C-H), calcium aluminate silicate hydrate (C-A-S-H), and calcium aluminate hydrate (C-A-H) [14–16]. Furthermore, the production of 1 ton cement produces 0.82 ton CO<sub>2</sub> whereas 1 ton CC produces 0.175 ton CO<sub>2</sub> emissions. Therefore, replacing 50% OPC with CC and LS reduces the carbon footprint up to 40% [22–24], which makes the binder low-carbon/cost and also an environmentally friendly alternative material [24-28]. Although the influence of LC<sup>3</sup> is validated for Zn alone, its effectiveness and mechanism involved for the immobilization of Zn and Pb when they co-exist are unknown and need additional investigations.

$$Al_2O_3(SiO_2)_2 \cdot (H_2O)_2 (Kaolinite) \rightarrow Al_2O_3(SiO_2)_2 \cdot (H_2O)_x (calcined \ clay) + (2-x)H_2O.$$
(1)

The objective of the study was to evaluate the feasibility of the LC<sup>3</sup> binder upon S/S of Znand Pb-contaminated soils individually as well as combined at elevated levels in terms of strength, toxicity leaching, chemical speciation, and XRPD analysis. The research aimed to provide scientific insights on environmentally friendly alternative LC<sup>3</sup>, such as: (1) to investigate the immobilization mechanisms involved in the soils treated with Zn and Pb; (2) to study the effect of curing time and binder dosage on physical strength and pH; and (3) to elucidate the hydration products responsible for the S/S of treated soils. This study provides the feasibility of using a sustainable binder LC<sup>3</sup> for the treatment of contaminated soils, while the treated soil can be reused as safe and environmentally friendly construction material.

#### 2. Materials and Methods

#### 2.1. Materials

Clean soil used in this study was collected from the nearby open area at Sardar Vallabhbhai National Institute of Technology, Surat, India. Approximately 250 kg of the soil sample was collected from the 0.5–1.0 m depth. Later, soil was homogenized, then air dried and passed into a 2 mm screen before use. The soil was classified as CH as per the Unified Soil Classification System based on ASTM D2487 [29], where initial water content, specific gravity, and pH were 19.7, 2.59, and 6.8, respectively, and the detailed chemical composition of the clean soil is shown in Table 1. Further, the binder  $LC^3$  was procured from Technological Action and Rural Advancement (TARA), Delhi, India and the major oxides present were CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> of 61.4%, 24.38%, 6.52%, and 4.31%. In addition, the remaining physicochemical parameters of soil and chemical composition of  $LC^3$  binder used in the study can be found in authors' previous study [21].

Table 1. Chemical composition of clean soil used in the study.

| Oxide                               | Value (%) <sup>a</sup> |  |  |  |
|-------------------------------------|------------------------|--|--|--|
| Silicon oxide (SiO <sub>2</sub> )   | 54.26                  |  |  |  |
| Aluminium oxide $(Al_2O_3)$         | 17.86                  |  |  |  |
| Ferric oxide ( $Fe_2O_3$ )          | 12.17                  |  |  |  |
| Calcium oxide (CaO)                 | 4.24                   |  |  |  |
| Magnesium oxide (MgO)               | 7.17                   |  |  |  |
| Potassium oxide ( $K_2O$ )          | 0.06                   |  |  |  |
| Titanium oxide (TiO <sub>2</sub> )  | ND <sup>c</sup>        |  |  |  |
| Sulphur trioxide (SO <sub>3</sub> ) | 1.28                   |  |  |  |
| Loss on ignition <sup>b</sup>       | 2.67                   |  |  |  |

<sup>a</sup> Analyzed using Rigaku WD-XRF machine. <sup>b</sup> Value of loss on ignition is referred to as 950 °C. <sup>c</sup> Not Detected.

## 2.2. Artificially Contaminated Soil and S/S Samples Preparation

The target metals used in the study were lead (Pb) and zinc (Zn) as they are considered as the most commonly encountered heavy metals at contaminated sites worldwide [15,18]. The analytical grade zinc nitrate hexa-hydrate Zn (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and lead nitrate hexa-hydrate Pb (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O were used and nitrate anion was chosen because it is inert and also eliminates unexpected precipitates with other ions during hydration and pozzolanic reaction [5,15]. Further, the essential volume of stock solutions was added to the air dried soil until the stock solution content reached to 29%, i.e., the optimum moisture content (OMC) of the soil, and then stayed untouched for 14 days to ensure the necessary contact between soil and heavy metals Pb and Zn. Similar procedure for the preparation of artificially contaminated soil was reported by Du et al. [18,30]. Further, the concentrations of 5000 mg/kg and 10,000 for both Zn and Pb and the combination of both at 10,000 mg/kg were used to represent typical field concentration levels. In addition, for comparison purposes, the untreated soil concentration was maintained at 10,000 mg/kg. The samples were designated as ZnU, PbU (untreated Zn and Pb), and Zn 0.5, Zn 1.0, Pb 0.5, Pb 1.0, and ZnPb 1.0 in the study. Furthermore, the binder LC<sup>3</sup> was added to artificially contaminated soil on predetermined dry soil weight basis at 8%. The soil–binder mixture was thoroughly mixed using an electronic mixer for 5–10 min in order to obtain a homogenous mix,

until the water content reached a predetermined OMC and maximum dry density (MDD), which are shown in Table 2. The mixture was compacted in three layers of 5 cm-diameter and 10 cm-height PVC molds using a hydraulic jack until it reached the MDD. The molds were carefully sealed in a polythene bags and demolded after curing periods of 3,7,14, 28, and 56 days. The mixing, curing, and compaction procedures were followed as per ASTM C192 [31] to ensure the similarity among all the samples.

| Sample Designation | OMC (%) | <b>MDD</b> (kg/m <sup>3</sup> ) |
|--------------------|---------|---------------------------------|
| ZnU                | 29      | $1.47 \times 10^{3}$            |
| PbU                | 29      | $1.46 \times 10^{3}$            |
| Zn 0.5             | 32      | $1.42 \times 10^{3}$            |
| Zn 1.0             | 33      | $1.43 \times 10^{3}$            |
| Pb 0.5             | 32      | $1.43 \times 10^{3}$            |
| Pb 1.0             | 33      | $1.43 \times 10^3$              |
| ZnPb 1.0           | 33      | $1.44 \times 10^{3}$            |

**Table 2.** Maximum dry density (MDD) and optimum moisture content (OMC) of untreated and 8% limestone-calcined clay cement (LC<sup>3</sup>)-treated Zn- and Pb-contaminated soils.

## 2.3. Testing Methods

The primary objective of the study was to determine the mechanical strength, leaching, chemical speciation, and mineralogy of the untreated and LC<sup>3</sup>-treated specimens. Physical strength was determined using an unconfined compression strength (UCS) test as per ASTM D2166 [32] with a controlled strain rate of 1%/minute. Later, the crushed samples were taken for determination of leaching, chemical speciation, and mineralogy tests. In addition, pH values were measured in the leachate by using HANNA waterproof tester, as per ASTM standard [33].

Toxicity leaching was performed as per standard toxicity characteristic leaching protocol (TCLP) EPA method 1311 [34]. In total, 10 g of the soil was mixed in TCLP fluid#1, i.e., CH<sub>3</sub>COOH and NaOH mixture at pH 4.93  $\pm$  0.05, and the soil solution mixture was rotated for 18  $\pm$  2 h at 30 rpm using an end-to-end shaker. Later, the leachant solution was separated using centrifuging/decantation at 3000 rpm for 8–10 min. Finally, the leachate was subjected to pH analysis and acidified using HNO<sub>3</sub> at (pH  $\leq$  2) before proceeding to heavy metal analysis. All the samples were tested in triplicates/quadruplicates for ensuring the repeatability of results, and average values of the results are reported in the study. In addition, to understand the leaching performance, S/S efficiencies of heavy metals [35] were determined using Equations (2) and (3), where S represents S/S efficiency and L is the leaching factor, which is defined by heavy metal concentration in leachate divided by the initial soil contamination condition.

$$S = 100 - L \tag{2}$$

$$L = \frac{Mass \ of \ contamination \ in \ leachate \ (mg)}{Initial \ mass \ of \ soil \ contamination \ (mg)} * 100.$$
(3)

Further, the chemical speciation analysis was performed using a modified Community Bureau of Reference three step sequential extraction procedure (BCR-SEP) [36–38]. The test method was comprised of four phases P1 = acid soluble phase, extraction in 0.11 mol/L CH<sub>3</sub>COOH at pH 2.8; P2 = reducible phase, extraction in 0.5 mol/L NH<sub>2</sub>OH·HCl at pH 1.5; P3 = oxidizable phase, oxidation in acid using 30% H<sub>2</sub>O<sub>2</sub> and extraction in 1 mol/L in CH<sub>3</sub>COONH<sub>4</sub>, both at pH 2; and P4 = residual phase, extraction with total digestion using mixture of (3:1) concentrated 70% HNO<sub>3</sub> and 30% HCl using 11,466 protocols [39]. Furthermore, the P1 phase was comprised of heavy metals that were precipitated and co-precipitated in a carbonate phase, which were present in a bioavailable form. The P2 phase was made-up of iron (Fe) and manganese (Mn) oxides that can be activated in high pH conditions (acidic). The P3 phase was incorporated into a stable organic matter and sulfides that were mobilizable and not bioavailable during oxidation. The P4 phase contained primary and secondary minerals, which could hold the heavy metals within the crystal lattices [2,38]. The P4 phase was

expected to remain for longer periods in the contaminated soil and very difficult to release, even at high pH conditions. In addition, to measure the reliability of sequential extraction procedure, metal recovery rate (MRR), given in Table 4, is the most commonly used parameter [38,40]. It is defined as the sum of four phases divided by total concentration obtained from the complete digestion as presented in Equation (4).

$$MRR(\%) = \frac{P1 + P2 + P3 + P4}{\text{Total Concentration}} \times (100).$$
(4)

Moreover, XRPD analysis was performed after hydration stoppage in the treated samples. The samples were powdered using 75  $\mu$ m mesh and tested using a Rigaku X-ray diffractometer with (Cu-K $\alpha$ ) radiation  $\lambda = 1.540538$  Å at the 2 $\theta$  (Theta) of 10°–70° with the step size of 0.02° under room temperature conditions. The system was operated at 45 kV and 30 mA, with a scan time of 20 s at each step in the step scan mode, and XRPD results were analyzed using PANanlytical Xpert High Scom<sub>1</sub>re plus software V.3e (Malvern Panalytical, Worcestershire, United Kingdom) [41] for attaining phase identification of minerals.

#### 3. Results and Discussion

#### 3.1. Leachate pH

Figure 1 represents the leachate pH of Zn- and Pb-treated soil with varying curing periods. It can be seen that LC<sup>3</sup> treatment significantly increased by approximately 1.3–2.4 and 1.1–1.4 units, respectively, for Zn and Pb at 7 days of curing as compared to untreated soil. However, Pb failed to reach the remediation goal compared to Zn. This may be due to the molar concentration of Pb, which is much lower than that of Zn, which induces more significant retardant effect on hydration in the system. For instance, at 28 days, mean pH values increased from 8.33 to 9.12 and 7.22 to 7.94, i.e., 2.66–3.45 and 1.98–2.7 units for Zn and Pb, respectively. Further, it can be noted that the pH values of Pb 1.0 and ZnPb 1.0 showed similar trends, which indicates Pb at higher concentrations retards the hydration mechanism in the system, which agrees well with Wang et al. and Xia et al. [17,42]. Furthermore, the increase in the pH values was noted at 56 days curing time by 8.71–9.36 and 7.37–8.38, which is 3.06–3.71 and 3.17–2.16 units. The increase in the pH values is attributed to the chemical composition of the binder, which facilitates the release of  $OH^-$ ,  $Ca^+$ , and  $Al^+$  ions in the pore water, creating an alkaline environment in the system [43,44]. Further, the dissolution of aluminates and silicates expedite the pozzolanic reaction over time, which are responsible for the binding of heavy metals to form insoluble metal hydroxides [24,45,46]. Therefore, the increase in pH over time in the treated system supports the formation of various hydration products, such as [ZnAl(OH)<sub>2</sub>(SO)<sub>2</sub>], [Pb<sub>2</sub>O(CO<sub>3</sub>)], [Ca(OH)<sub>2</sub>], Ca<sub>3</sub>O<sub>5</sub>Si, [CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>], (Aft) [Ca<sub>6</sub>Al<sub>2</sub>(SO4)<sub>3</sub>(OH)<sub>12</sub>.26H<sub>2</sub>O], and [CaCO<sub>3</sub>], which is also validated by XRPD analysis Section 3.5 in the study.

#### 3.2. Zn and Pb Leachability

Figure 2 shows the leached Zn and Pb concentrations in the TCLP test. It was observed that leached Zn and Pb concentrations exceeded Hazardous Waste Management (HWM) rules [47] limits of Zn (250 mg/L) and Pb (5 mg/L), respectively, suggesting that the soil is toxic and requires remediation. The average leached concentrations of  $LC^3$ -stabilized soils decreased with the rising curing time. Besides, the leached Zn concentrations were below regulatory limit after 14 days of curing. Whereas, Pb reached the regulatory limit only after 28 days of curing, showing the solidification efficiency of approximately 88% and 99% with leaching factors 11.89 and 1.22 for Zn and Pb. The decrease in the leached concentrations could be due to increased pH values in the previous Section 3.1 and formation of metal hydroxides in the presence of freely available Ca (OH)<sub>2</sub> and Ca<sup>+</sup> ions in the binder [43]. Moreover, LS, when added with CC, reacts to form carbo-aluminates, which produces C-S-H and C-A-H-based hydration products that have a tendency to arrest the heavy metals in forming insoluble

metal hydroxides that increase the immobilization efficiency and reduce leaching. Overall, it can be concluded that LC<sup>3</sup> stabilization promotes the immobilization of Zn- and Pb-contaminated soils, which further reduces leachability.



**Figure 1.** pH of the untreated and LC<sup>3</sup>-treated soils with varying curing periods.



**Figure 2.** Toxicity characteristic leaching protocol (TCLP) of leached Zn and Pb concentrations with varying curing times.

#### 3.3. Unconfined Compressive Strength

Figure 3 represents the unconfined compressive strength behavior of  $LC^3$ -treated samples with varying curing time. In all the treated samples, increasing compression strength was observed over untreated soil with curing time. However, Pb has the retardation effect on the treated soil at higher concentrations, which ultimately decreases the strength values. For instance, the increase in the strength values of  $LC^3$ -treated soil was approximately 1.50–1.62 and 2.42–2.57 for Zn, whereas 1.46–1.69 and 2.46–2.94 for Pb at 7 and 28 days of curing, and the additional values can be found in Table 3. Moreover, it was seen that increases in the strength values were observed even after 28 days of curing, which is because  $LC^3$  can improve strength even up to 365 days of curing [48] as a consequence of hydration reactions [45,49]. In addition, binder  $LC^3$  includes partial replacement of cement with calcined clay and limestone, and during the hydration process the combination of Ca (OH)<sub>2</sub> and CC increases the pozzolanic reactivity [24,28,41,43,50], which produces more binding phases, resulting in improved density and reduced pore spaces that ultimately lead to increased compressive strength. Therefore, the results demonstrate that Zn and Pb concentrations at higher levels have synergetic effects that could favorably affect the strength behavior of contaminated soils.



Figure 3. Compressive strength results of the untreated and LC<sup>3</sup>-treated soil with varying curing period.

| Table 3. | Unconfined of | compressive strer | ngth values o | of initial soil | contamination | condition and | curing time. |
|----------|---------------|-------------------|---------------|-----------------|---------------|---------------|--------------|
|          |               |                   | 0             |                 |               |               |              |

| Initial Soil Contamination Condition | 7.11   | J PbU  | 7.05    | Zn 1.0  | Pb 0.5  | Pb 1.0  | ZnPb 1.0 |
|--------------------------------------|--------|--------|---------|---------|---------|---------|----------|
| Curing (Days)                        | ZnU    |        | Zn 0.5  |         |         |         |          |
| 3                                    | -      | -      | 599.65  | 586.35  | 422.54  | 394.22  | 447.35   |
| 7                                    | -      | -      | 689.67  | 638.37  | 569.54  | 492.33  | 587.26   |
| 14                                   | -      | -      | 812.34  | 754.32  | 733.51  | 688.34  | 713.35   |
| 28                                   | 423.35 | 336.84 | 1089.38 | 1025.37 | 986.82  | 829.64  | 1121.67  |
| 56                                   | -      | -      | 1364.38 | 1296.35 | 1195.24 | 1027.33 | 1142.54  |

Note: Units for compressive strength values are (kPa).

#### 3.4. Chemical Speciation of Heavy Metals

Typically, four phases of soil sample are analyzed to recognize the environmental activity and bioavailability of heavy metals, namely acid soluble (P1), reducible (P2), oxidizable (P3), and residual phases (P4). Commonly, P1 and P2 phases are considered to be bioavailable in nature due to their weak binding capacity in the acidic/low pH environment [38]. The higher the proportion of P1 and P2 in an active fraction, the greater the heavy metal's ion mobility [36,51,52]. Therefore, the phases P1 and P2, particularly the P1 phase, are not stable and impose environmental risks resulting from leached heavy metals in the environment. Further, to assess the reliability of the phase extractions, the metal recovery rate (MRR) is given in Table 4. Figure 4a,b shows the histograms of Zn and Pb metal distribution after LC<sup>3</sup> treatment at 28 and 56 days of curing. As shown in Figure 4a, the P1 of Zn in LC<sup>3</sup>-stabilized soil was 21–32% lower than 61% of ZnU (untreated Zn) and approximately 37–51% of Zn in the stabilized soil was bound to the P4 phase. Besides, the P1 phase of Pb in the  $LC^3$ -stabilized soil ranged from 33–46% lower than 58% of PbU (untreated Pb), and 36–44% of Pb in the stabilized soil was bound to the P4 phases after 28 days of curing. While at 56 days of curing, as shown in Figure 4b, the increase in the P4 phase in the stabilized soil ranged from 53-67% and 41-58% for Zn and Pb, respectively. The increase in the P4 phase thus promotes the development of highly insoluble and immobile complexes that are responsible for making the heavy metals less bioavailable in nature under low pH/acidic environmental conditions. It can be concluded that LC<sup>3</sup> stabilization/solidification results in the transformation of (acid-soluble) P1 phases of Zn- and Pb-contaminated soil into more insoluble (residual) P4 phases.

Table 4. Metal recovery rate (MRR) after modified BCR-sequential extraction test.

| Sample Designation         | ZnU | PbU | Zn 0.5 | Zn 1.0 | Pb 0.5 | Pb 1.0 | ZnPb 1.0 |
|----------------------------|-----|-----|--------|--------|--------|--------|----------|
| Metal recovery rate (MRR%) | 91  | 82  | 86     | 93     | 88     | 94     | 95       |

#### 3.5. XRPD Analysis

The mineralogical analysis was conducted after 28 days of curing for both untreated and LC<sup>3</sup>-treated samples to examine the effect of hydration and pozzolanic reaction on various phases of the contaminants, i.e., Pb and Zn in a stabilized matrix, as shown in Figure 5. The results show quartz [SiO<sub>2</sub>], muscovite [(KF)<sub>2</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>3</sub>(SiO<sub>2</sub>)<sub>6</sub>(H<sub>2</sub>O)], albite [NaAlSi<sub>3</sub>O<sub>8</sub>], wulfingite [Zn(OH)<sub>2</sub>], zinc silicate [Zn<sub>2</sub>SiO<sub>4</sub>], and lead silicate [Pb<sub>2</sub>SiO<sub>3</sub>] were the primary minerals in the untreated Zn and Pb soil. Whereas hydration products such as zincwoodwardite [ZnAl(OH)<sub>2</sub>(SO)<sub>2</sub>], shannonite  $[Pb_2O(CO_3)]$ , portlandite  $[Ca(OH)_2]$ , haturite  $Ca_3O_5Si$ , anorthite  $[CaAl_2Si_2O_8]$ , ettringite (Aft)  $[Ca_6Al_2(SO4)_3(OH)_{12}.26H_2O]$ , and calcite  $[CaCO_3]$  were the major cementitious products responsible for stabilization in the treated samples and these hydrated products controlled the heavy metal migration in the  $LC^3$  samples, which agrees well with Wang et al. [48]. The formation of aluminates and silicates-based products after  $LC^3$  treatment was also noticeable, which was due to the availability of carbo-aluminate phases in the hydroxyl-rich calcined clay and limestone [24,28,46]. The changes in the structural and crystalline phases were due to lime, which is effectively activated by calcined clay, which further enhances metal hydrates and hydroxide phase formation. Accordingly, these products are normally insoluble, promoting Zn and Pb immobilization, which improves soil stabilization and reduction in the leaching of contaminated soils.



**Figure 4.** Distribution of heavy metals in the untreated and LC<sup>3</sup> treated soils after (**a**) 28 days (**b**) 56 days of curing.



**Figure 5.** X-ray powder diffraction (XRPD) analysis of untreated and LC<sup>3</sup>-treated soils after 28 days of curing.

#### 4. Conclusions

The present study investigated the role of  $LC^3$  on Zn- and Pb-contaminated soils and evaluated the S/S performance through analyses of unconfined compressive strength, chemical speciation, leaching, and XRD. XRD results showed that Zn and Pb had become an integral part of the crystalline phase physically and chemically in forming Si- and Al-based carbo-alumino-silicate products such as Ca(OH)<sub>2</sub>, Ca<sub>3</sub>O<sub>5</sub>Si, CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>, and Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>.26H<sub>2</sub>O (Aft), which were responsible for the immobilization of heavy metals. The compressive strength results indicated that the addition of the LC<sup>3</sup> binder at 8% could improve the strength values up to three times compared to untreated Zn- and Pb-contaminated soils. The pH transformation of acidic to alkaline nature after a 14 day curing period allowed the adsorption of heavy metals in forming various insoluble metal hydroxides. Leachability of Zn-contaminated soil reached the regulatory limit after 14 days of curing, whereas Pb-contaminated and mixed contaminated soil, ZnPb, reached the limit only after 28 days of curing. Chemical speciation results indicated that reduction in the acid-soluble phases and increased residual phases significantly supported the formation of insoluble hydration products, which were responsible for increased immobilization efficiency and strength. The results illustrated that LC<sup>3</sup> is a promising binder in solidifying/stabilizing the contaminated soils and the treated soils can be reused as safe and sustainable construction materials.

**Author Contributions:** V.A.R., laboratory investigation, result analysis, writing—original manuscript; C.H.S. and S.K., supervision, writing—review and editing; K.R.R., conceptualization, supervision, writing—review and editing; Y.-J.D. writing—review and editing. All authors have read and agreed to the current version of the manuscript.

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