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Assessment of the Stabilization of Cu-, Pb-, and Zn-Contaminated Fine Soil Using Cockle Shells, Scallop Shells, and Starfish

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Abstract: Soil washing is a well-established remediation technology for treating soil contaminated with heavy metals. It involves the separation of contaminants from the soil using acidic washing agents. Nevertheless, the application of washing agents at high concentrations may lead to soil acidification and the destruction of the clay structure. To avert this problem, recently, a soil washing variant has been presented, which solely employs high-pressure water without any chemical solvents. However, the fine soil generated from soil washing at a high-pressure contains high levels of heavy metals and requires proper treatment. This study examines the use and applicability of natural aquaculture materials as stabilizing agents for treating heavy metals (Cu, Pb, and Zn) in fine soil generated by high-pressure soil washing. Three aquaculture materials were assessed, namely, cockle shells (CKS), scallop shells (SLS), and *Asterias amurensis* starfish (ASF). Each material was processed to yield three types of stabilizing agents: natural type (-#10 mesh), natural type (-#20 mesh), and calcined(C) type (-#10 mesh). Each stabilizing agent was added to the contaminated soil at a ratio of 0 to 10 wt%, and then, mixed with an appropriate amount of water. After wet curing for 28 days, the stabilization efficiency of Cu, Pb, and Zn was evaluated using 0.1 N HCl solution. The elution of heavy metals showed a decreasing trend with higher dosages of stabilizing agents. The calcined type (-#10) showed the highest stabilization efficiency, followed by the natural type (-#20) and natural type (-#10). In addition, a comparison of the efficiency of the different stabilizing agents showed that calcined ASF (CASF) had the highest stabilization efficiency, followed by calcined SLS (CSLS), calcined CKS (CCKS), natural ASF (NASF), natural SLS (NSLS), and natural CKS. Finally, analysis of samples exhibiting the highest stabilization efficiency by scanning electron microscopy–energy dispersive X-ray spectrometry (SEM–EDX) confirmed that the pozzolanic reaction contributed to the stabilization treatment. The results of this study demonstrate that heavy metal-contaminated fine soil, generated by high-pressure washing, can be remediated by stabilizing Cu, Pb, and Zn using waste aquaculture materials (CKS, SLS, and ASF), which are often illegally dumped into the sea or landfills and cause environmental damage.

Keywords: stabilization; immobilization; cockle shells; scallop shells; starfish

1. Introduction

Soil contamination by heavy metals is an environmental concern worldwide [1]. Heavy metals are conservative contaminants that upon entrance to the food chain can cause adverse environmental and human health effects [1,2]. Soil washing, a remediation technique for soil contaminated with heavy metals, has been widely applied worldwide owing to its ability to remove heavy metals with high efficiency by using chemical washing agents, such as HCl, HNO₃, EDTA, CaCl₂, oxalate, NaCl, etc., depending on the type of contaminant [3,4]. Soil washing typically involves physical separation and chemical extraction.

Following physical separation, heavy metals are removed from the contaminated soil, or the volume of contaminated soil is reduced through chemical extraction [3]. Various acidic washing agents, including hydrochloric acid, are used to remediate heavy metal-contaminated soils, although often cause deterioration of the soil quality [5,6]. Research to address this issue includes the use of high acidity and low silica dissolution rate washing agents, such as $FeCl_3$, to reduce the destruction of clay minerals caused by hydrochloric acid and increase the heavy metal washing effect [6,7]. $FeCl_3$, which is an inorganic acid, has also been found to induce soil acidification by decreasing the pH of the remediated soil to ≤ 4 after washing [7,8].

Recent studies to tackle the shortcomings of conventional acid washing have investigated high-pressure soil washing, which prevents soil acidification and maximizes the physical washing effect by solely using high-pressure water [9,10]. High-pressure soil washing involves the restoration of heavy metal-contaminated soil by dispersing soil aggregates to reduce large particles into small particles through high-pressure water injection and separating only the fine soil contaminated with elevated levels of heavy metals [11]. This method aids in reducing the volume of contaminated soil and obtaining remediated soil by separating the contaminated fine soil fraction soil without chemical washing agents [9,11]. However, direct disposal of the fine soil poses a challenge owing to its high levels of heavy metal contamination. In addition, since it is difficult to remove heavy metals from soils with small particles (i.e., fine soil), even by chemical washing agents, proper treatment is required [3,12].

Stabilization technology aids in immobilizing and reducing the bioavailability of heavy metals by adding stabilizing agents to contaminated soils [13]. Stabilization technology cannot eliminate heavy metals from the soil but can reduce probable environmental and human health risks. The technology is known for its applicability to diverse soil types and heavy metal contaminants, offering substantially high restoration reliability and economic efficiency. Industrial byproducts, such as Portland cement, cement kiln dust, and fly ash, have been commonly used as stabilizing agents [14–17]. Recently, however, low-cost, available, and sustainable stabilizing agents, including natural waste resources, agricultural byproducts, and natural materials, have been used worldwide [18–20]. This study reports on the use of marine byproducts with a high calcium carbonate content (cockle shells: CKS; scallop shells: SLS; *Asterias amurensis* starfish: ASF) as stabilizing agents of heavy metal-contaminated fine soils.

High quantities (>10 million tons) of mollusk shells are generated globally every year, and more than 70% are shells of oysters, clams, scallops, and mussels [21]. These shells are mostly dumped into the sea or landfills. However, without proper control, they cause environmental degradation manifested with malodorous emissions and/or visual pollution. In Korea, a law to promote the recycling of six types of shellfish (oysters, clams, abalones, pen shells, mussels, and cockles) has been implemented since July 2022, aimed at the reutilization of previously discarded shells. Among these, SLS and CKS, which have limited research precedent in the context of heavy metal stabilization, were used as stabilizing agents. Approximately 200 species of starfish, a major predator of these shellfish, inhabit the Korean coasts. Representative species include the Northern Pacific starfish *Asterias amurensis*, and *Asterina pectinifera*. These two species, in particular, cause economic damage to aquaculture, and thus, are designated as harmful marine organisms in Korea. Therefore, ASF were used as a stabilizing agent, and its treatment efficiency was assessed.

The objective of this study was the stabilization of the heavy metals in contaminated fine soil generated after high-pressure washing with CKS, SLS, and ASF, to subsequently evaluate their effectiveness. Firstly, the effect of each agent on heavy metal (Cu, Pb, and Zn) stabilization was compared and analyzed according to the particle size (-#10 and -#20 mesh) and the presence/absence of calcination. In addition, scanning electron microscopy–energy dispersive X-ray spectrometry (SEM–EDX) analysis was conducted on the soil treated with various stabilizing agents to identify the main stabilization mechanisms. Finally, CKS, SLS, and ASF were recycled as stabilizing agents for heavy metal-contaminated fine soil, and their efficiency was evaluated.

2. Experimental Methodology

2.1. Collection of Contaminated Fine Soil

The sample used in this study comprised the fine soil generated from high-pressure washing. To evaluate the characteristics of the fine soil, it was completely dried at 105 °C and sifted using a standard sieve of 10 mesh (2 mm). The collected soil was referred to as concentrated soil (CS). The pH, EC, and organic matter content were measured to evaluate the characteristics of CS (Table 1). The total concentrations of copper, lead, and zinc in CS were 667.7, 514.6, and 852.7 mg/kg, respectively. Analysis of the particle size distribution revealed that the soil type was sandy clay (sand: 54.1%, silt: 0.5%, and clay: 45.4%). The XRF analysis results for CS are shown in Table 2.

Table 1. Soil characterization results.

Soil Properties	Contaminated Soil	Regulatory Limit [a]
Soil pH	5.91	
EC (μS/m)	0.58	
Organic matter content (%) [b]	3.84	
Composition (%) [c]		
Sand	54.1	
Silt	0.5	
Clay	45.4	
Texture [d]	Sandy clay	
Heavy metals ($mg \cdot kg^{-1}$)		
Cu	667.7	150 (Korean warning standard)
Pb	514.6	200 (Korean warning standard)
Zn	852.7	300 (Korean warning standard)
Major mineral compositions	Quartz, Muscovite, Albite, Montmorillonite, Kaolinite	

[a] Korean warning standard for soils in region 1 (residential area); [b] organic matter content (%) was determined by measured loss-on-ignition (LOI); [c] Soil size distribution was determined by particle size analysis (PSA); sand: 20–2000 μm; silt: 2–20 μm; clay: <2 μm; [d] soil texture was assessed as per United States Department of Agriculture (USDA).

Table 2. Major chemical composition of concentrated soil, NCKS, NSLS, NASF, CCKS, CSLS, and CASF.

Major Chemical Composition (%)	Contaminated Soil	NCKS	NSLS	NASF	CCKS	CSLS	CASF
SiO_2	57.43	1.23	0.073	0.159	0.129	0.113	0.126
Al_2O_3	26.74	0.475	0.209	0.061	0.041	0.154	0.130
Na_2O	0.824	1.10	0.841	2.55	1.07	0.974	2.51
K_2O	3.02	0.098	0.008	0.419	0.020	0.012	0.158
CaO	1.55	94.93	96.53	79.77	96.92	96.18	78.78
Fe_2O_3	6.14	0.389	0.066	0.081	0.067	0.051	0.052
SO_3	0.187	0.704	0.609	6.47	0.261	0.580	2.45
MnO	0.109	0.157	0.007	0.009	0.024	0.007	0.004
P_2O_5	0.484	0.172	0.124	1.42	0.045	0.129	0.633
pH (1:5)	5.91	9.40	9.42	7.37	12.45	12.51	12.29

2.2. Stabilizing Agents

This study used CKS, SLS, and ASF as stabilizing agents. CKS and SLS were purchased from a nearby market, and ASF was collected from the coast of Jeju Island. Firstly, CKS, SLS, and ASF were cleaned to eliminate foreign matter, and then, immersed in flowing water for 3 days to remove any salt. Next, they were washed several times with distilled water, naturally dried, and crushed using a mixer. Next, they were sifted through #10 mesh (2 mm), and the resulting stabilizing agents were referred to as -#10 mesh natural cockle shells (NCKS10), natural scallop shells (NSLS10), and natural *Asterias amurensis* starfish

(NASF10. In addition, the stabilizing agents obtained by crushing and sifting through #20 mesh were referred to as NCKS20, NSLS20, and NASF20. The main component of natural shells and starfish was $CaCO_3$, which is known to have low reactivity owing to the low solubility product constant [22]. Therefore, the stabilizing agents sifted through #10 mesh were placed in a furnace (900 °C; 2 h) to remove CO_2 and convert them into CaO with higher reactivity [22,23]. The converted CaO can dissociate quickly into Ca ions and offers more exchangeable sites for heavy metals than the non-calcined agents [24]. In particular, the calcined agents significantly increase the solubility of the silica and alumina present in clay minerals in strong alkaline environments, where the pH of the soil is above 12. Then, the silica and alumina can react with the Ca in CaO to form cementitious hydrates, which are considered to be responsible for heavy metal immobilization [25]. The resulting agents were referred to as -#10 mesh calcined cockle shells (CCKS10), calcined scallop shells (CSLS10), and calcined *Asterias amurensis* starfish (CASF10). The XRF analysis and pH results for each stabilizing agent are shown in Table 2.

2.3. Stabilization Experiments

For stabilization experiments, contaminated soil and the prepared stabilizing agents were mixed in a sealed container, and reactions were observed as water was added. To measure the efficiency of the stabilizing agents used according to their type and content, the natural stabilizing agents (NCK, NSLS, and NASF) of -#10 mesh and -#20 mesh and the calcined stabilizing agents (CCKS, CSLS, and CASF) of -#10 mesh were added into CS at 2, 4, 6, 8, and 10 wt%. Thereafter, 30 wt% of water was added to induce a hydration reaction, and the mixture was sufficiently agitated to ensure a homogeneous state. To observe the stabilization efficiency of the stabilizing agents according to the particle size and calcination reaction, the stabilizing agents were sifted through -#20 mesh, and the calcined stabilizing agents were also subjected to the same experiment. All samples were stored at room temperature in a sealed state to minimize the effect of carbonation caused by CO_2 in the atmosphere, and they were exposed to wet curing for 28 days. Table 3 shows the stabilization matrix for the entire experiment.

Table 3. Treatability matrix for heavy metal-contaminated fine soil.

Sample ID	Contaminated Soil (wt%)	Stabilizing Agent Dosage (wt%)	L:S Ratio
CKS/SLS/ASF 0 wt% (Control) CCKS/CSLS/CASF 0 wt%	100	0	30:1
CKS/SLS/ASF 2 wt% CCKS/CSLS/CASF 2 wt%	100	2	30:1
CKS/SLS/ASF 4 wt% CCKS/CSLS/CASF 4 wt%	100	4	30:1
CKS/SLS/ASF 6 wt% CCKS/CSLS/CASF 6 wt%	100	6	30:1
CKS/SLS/ASF 8 wt% CCKS/CSLS/CASF 8 wt%	100	8	30:1
CKS/SLS/ASF 10 wt% CCKS/CSLS/CASF 10 wt%	100	10	30:1

2.4. Heavy Metal Leaching Tests

Extraction with 0.1 N HCl was used to determine the stabilization efficiency based on the existing soil contamination test standard [26]. A 15 mL volume of 0.1 N HCl was applied to 3 g of soil, and the mixture was shaken at 100 rpm for 1 h at 30 °C using a constant temperature horizontal shaker. The mixture was collected with a syringe filter (<0.45 μm), and the filtered solution was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES).

2.5. X-ray Powder Diffraction (XRPD) Analysis

XRPD analysis was conducted to investigate the mineralogical characteristics of CS and stabilizing agents. The XRPD samples were dried, crushed, and sifted through a standard #200 mesh sieve (0.075 mm). The X-ray diffraction pattern was analyzed using an X-ray diffractometer (XRD) (X'Pert PRO MPD, PANalytical, Almelo, Netherlands) equipped with a diffraction beam graphite monochromator emitting Cu radiation at 40 kV and 40 mA. XRPD pattern collection was performed at 2θ range of 5–60°, 0.02° step size, and 3 s/step count time.

2.6. Scanning Electron Microscopy–Energy Dispersive X-ray Spectroscopy (SEM–EDX) Analysis

In this study, SEM–EDX was used to identify the effective heavy metal stabilization mechanisms in contaminated soil according to the addition of stabilizing agents. SEM–EDX analysis is mainly used to identify stabilization mechanisms since it can examine the images and constituent elements of the stabilized material [27–32]. Samples containing 10 wt% of CCKS10, CSLS10, and CASF10 were compared to the contaminated soil, which exhibited the highest stabilization efficiency, and selected as target samples. Air drying was performed before the analysis. The samples were attached to a tape coated with carbon on both sides and then coated with platinum under a vacuum for the analysis. Then, the constituent elements of the samples were identified using Hitachi S-4800 SEM equipment (Tokyo, Japan), equipped with a Horiba EMAX EDX system (Tokyo, Japan).

3. Results and Discussion

3.1. XRPD Analysis

Figures 1 and 2 show the XRD patterns of the contaminated fine soil and the NCKS, NSLS, NASF (a), CCKS, CSLS, and CASF (b) samples. The main mineral types in fine soil included quartz (powder diffraction file (PDF)# 46-1045), muscovite (PDF# 07-0025), albite (PDF# 09-10466), kaolinite (PDF# 29-1488), and montmorillonite (PDF# 13-0135). The main component in NCKS, NSLS, and NASF was $CaCO_3$. The mineral type in NCKS was aragonite (PDF# 41-1475), whereas that in NSLS and NASF was calcite (PDF# 47-1743, $CaCO_3$, PDF# 43-0697, $(Ca, Mg)CO_3$). The primary mineral type in CCKS, CSLS, and CASF, which are calcined stabilizing agents, was found to be quicklime (PDF# 48-1467, CaO). This demonstrates that a chemical decomposition reaction converts $CaCO_3$ into CaO during the calcination process (900 °C; 2 h) [33,34].
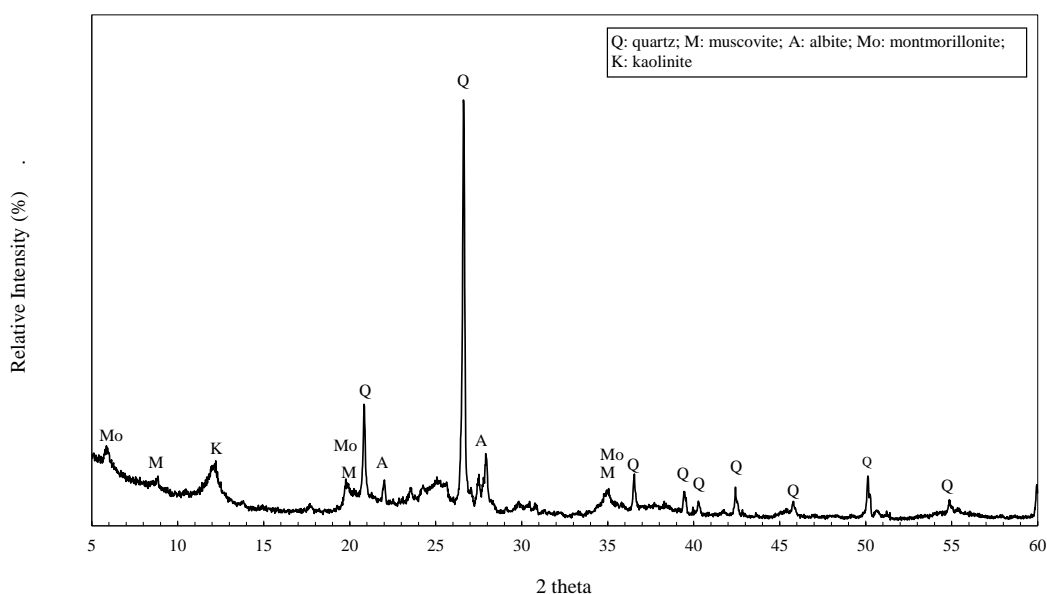
Figure 1. XRPD pattern of heavy metal-contaminated fine soil.
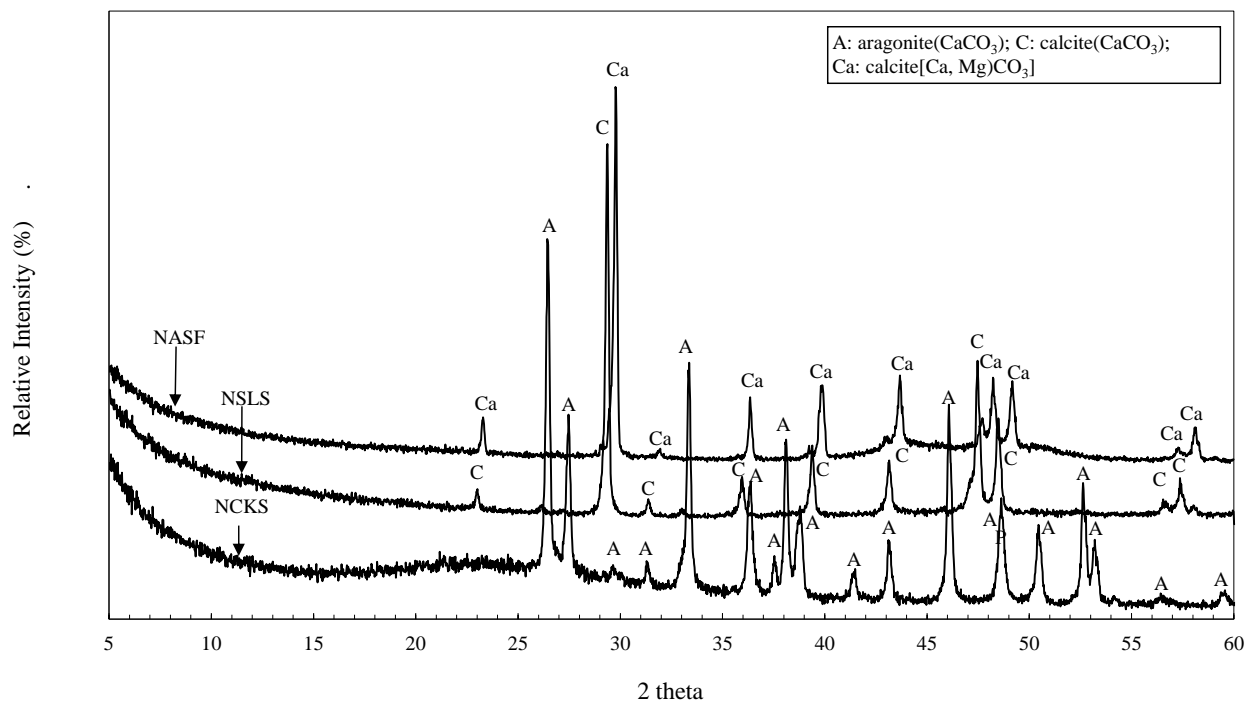
(**a**)
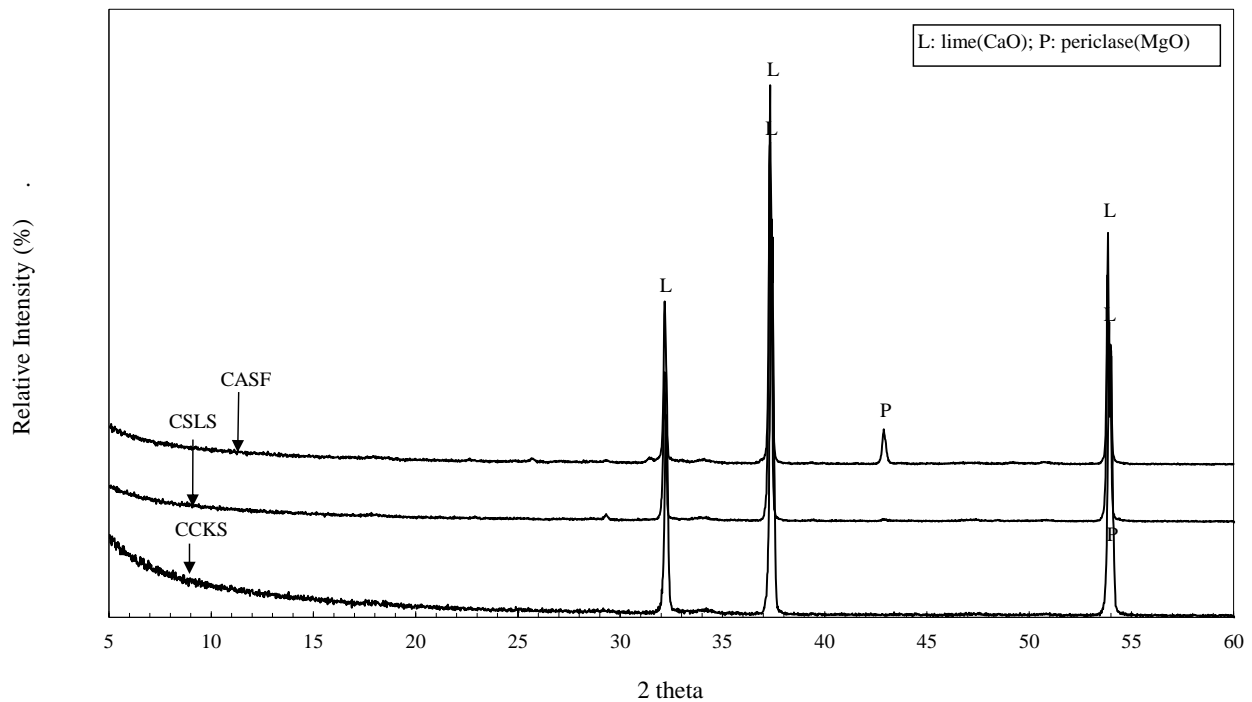
(**b**)

Figure 2. XRPD patterns of NCKS, NSLS, NASF (**a**), CCKS, CSLS, and CASF (**b**).

3.2. Effectiveness of the Stabilization Treatment

CKS, SLS, and ASF were processed into three types (-#10 mesh natural type, -#20 mesh natural type, and -#10 mesh calcined type) and added into contaminated soil, followed by wet curing for 28 days. Figures 3–11 show the stabilization efficiency graphs for Cu, Pb, and Zn extracted with 0.1 N HCl. As the dosage of the stabilizing agents increased, the

heavy metal stabilization efficiency also increased. The efficiency increased considerably when the stabilizing agent particle size was reduced, or the calcined stabilizing agents were applied. In addition, the stabilization efficiency of CKS, SLS, and ASF for each processing type was compared and evaluated. For CKS, NCKS10 was added to the soil at 10 wt%. Compared to the leaching concentrations of the control (Cu: 411.7, Pb: 284.8, and Zn: 306.3 mg/kg), maximum stabilization efficiency values of 92.8%, 97.8%, and 54.2% for copper (29.5 mg/kg), lead (6.2 mg/kg), and zinc (140.2 mg/kg) were observed, respectively (Figures 3–5). When NCKS20 was applied with a smaller particle size, the overall treatment efficiency was improved compared to NCKS10. In particular, following treatment with 10 wt% NCKS20, copper, lead, and zinc leaching concentrations were 15.3, 1.2, and 86.2 mg/kg, thereby increasing the treatment efficiency by approximately 3.5%, 1.8%, and 17.6%, respectively, compared to 10 wt% NCKS10 treatment (Figures 3–5). Moon et al. [23,33] also reported that the heavy metal stabilization efficiency increased as the stabilizing agent particle size decreased, confirming that reactivity with contaminated soil particles was improved as the surface area of stabilizing agents increased.
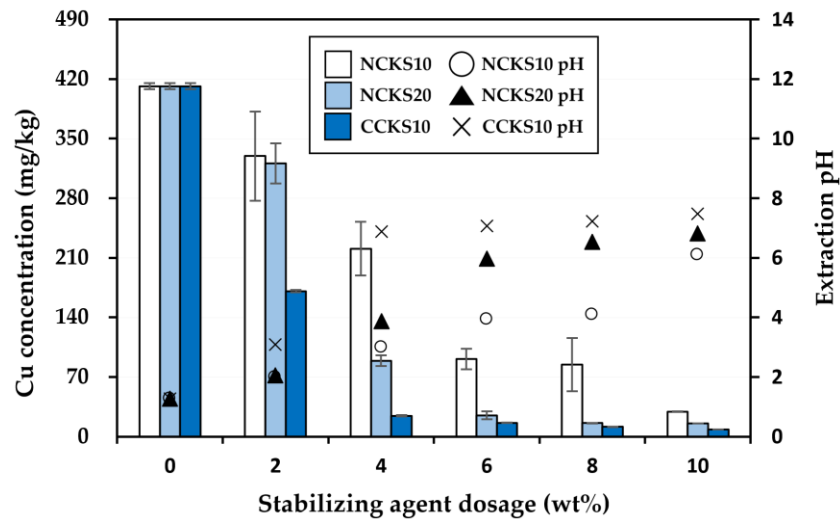

Figure 3. Cu concentrations under -#10 mesh NCKS, -#20 mesh NCKS, and -#10 mesh CCKS treatment after 28 days of curing, upon 0.1 N HCl extraction.
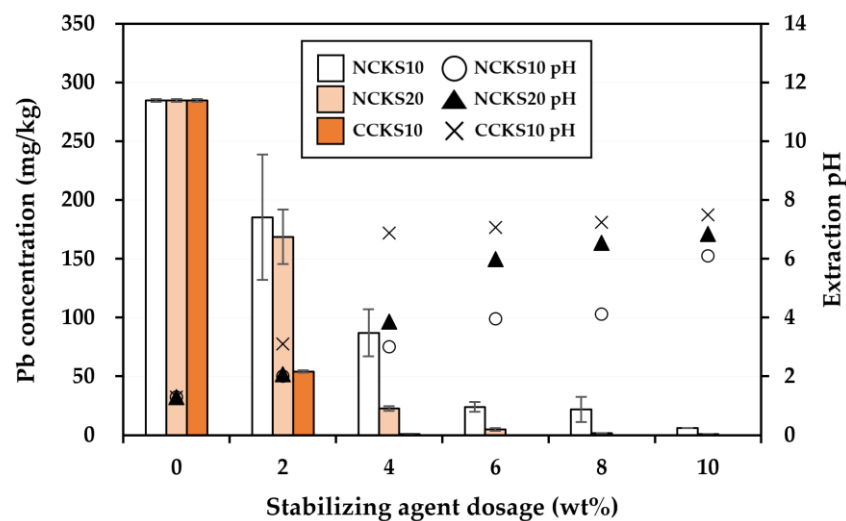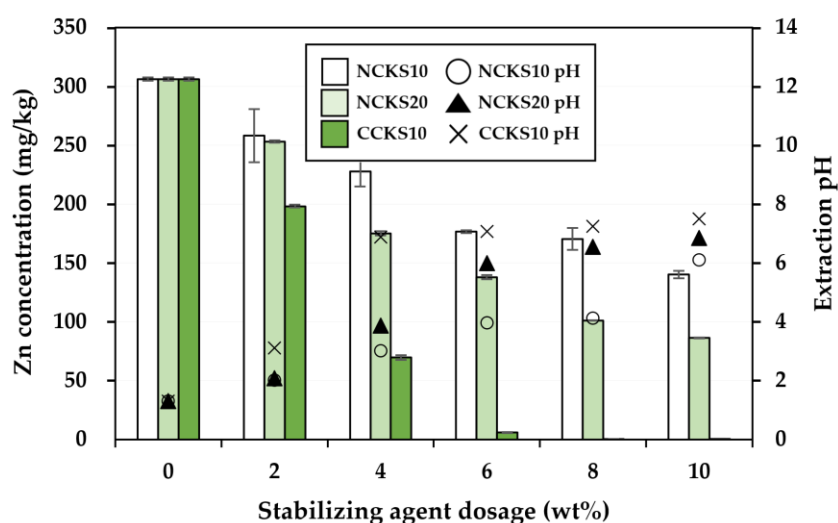

Figure 4. Pb concentrations under -#10 mesh NCKS, -#20 mesh NCKS, and -#10 mesh CCKS treatment (28 days curing; 0.1 N HCl extraction).

Figure 5. Zn concentrations under -#10 mesh NCKS, -#20 mesh NCKS, and -#10 mesh CCKS treatment (28 days curing; 0.1 N HCl extraction).

CCKS10 was applied to compare the treatment efficiency of the calcined CKS stabilizing agents. CCKS10 showed significantly higher treatment efficiency than NCKS. In particular, the application of only 4 wt% showed leaching concentrations of 24.6, 1.4, and 69.7 mg/kg for copper, lead, and zinc, respectively, resulting in similar leaching reduction efficiency to 10 wt% NCKS20 treatment (Figures 1–3). In addition, 10 wt% CCKS10 treatment exhibited the lowest leaching concentrations of 8.6 and 0.4 mg/kg for copper and zinc, respectively, while the extraction of lead was minimal (Figures 1–3). Islam et al. [27] added calcined CKS (-#20 mesh) into mine soil contaminated with Pb and Zn at 5 wt% compared to the contaminated soil and allowed curing for 28 days. They reported that the stabilization efficiency was 85% for Pb and 91% for Zn when extraction was performed using 0.1 N HCl. In the present study, 6 wt% CCKS10 treatment exhibited a leaching reduction efficiency of 99.9% and 98.1% for lead and zinc, respectively, facilitating effective heavy metal stabilization in the washed fine soil (Figures 4 and 5). It has also been reported that CCKS10 treatment considerably improves the stabilization efficiency and contributes to effective stabilization because its main component (CaO) forms stabilized substances of low solubility, such as calcium silicate hydrates (CSHs) and calcium aluminum hydrates (CAHs), along with heavy metals in the soil [30,33,35].

For SLS, compared to the initial leaching concentrations (Cu: 387.5, Pb: 264.1, and Zn: 306.3 mg/kg), 10 wt% NSLS10 treatment showed a maximum stabilization efficiency of 96.8%, 98.9%, and 64.7% in the order of copper (12.4 mg/kg), lead (2.9 mg/kg), and zinc (106.6 mg/kg), as shown in Figures 6–8. Similar to CKS, treatment using 10 wt% NSLS20 with a smaller particle size reduced the leaching concentrations of copper, lead, and zinc to 7.1, 1.4, and 75.0 mg/kg, respectively. This could be attributed to an active hydration reaction, which likely occurred due to the specific surface area increase caused by particle size reduction in the SLS, similar to the previous CKS treatment [22,34]. In addition, 10 wt% CSLS10 treatment showed the lowest leaching concentration of 5.7 mg/kg for copper, while lead and zinc were hardly extracted (Figures 6–8). This is because CaO, the main component in CSLS, precipitates heavy metals in soil by elevating the soil pH and effectively stabilizes heavy metals by generating pozzolanic materials with low solubility, such as CAHs and CSHs [27,28,30,32,36]. In addition, a comparison of the stabilization efficiency of CKS (Figures 3–5) to SLS (Figures 6–8) showed that SLS treatment reduced the leaching concentrations of copper, lead, and zinc slightly further, despite being the same shell. For example, based on a stabilizing agent dosage of 2 wt%, the treatment efficiency of NSLS10 was higher than for NCKS10 by 18.9% (Cu), 14.7% (Pb), and 8.8% (Zn). This could be attributed to the mineralogical characteristics of the shell types. Song et al. [37] reported that the main components of SLS and CKS were calcite and aragonite, respectively,

using XRD analysis. This was in agreement with the XRPD analysis results of the present study (Figure 2). In addition, according to the specific surface area analysis results for the same particle size (-#200 mesh), the specific surface areas of SLS and CKS were 4.2959 and 3.0143 m^2/g, respectively. A previous study reported that the shells that were heated at 100 °C for 10 min exhibited considerably higher specific surface area in SLS (4.5481 m^2/g) than in CKS (2.7241 m^2/g) [37]. Therefore, SLS could further increase the pH and heavy metal removal efficiency compared to CKS, when the heavy metals (i.e., Zn and Cd) are removed from the shell in an aqueous solution [37]. In the present study, the extraction pH of NSLS (7.3) was also slightly higher than for NCKS (6.8). This indicates that the stabilization efficiency of SLS is higher than that of CKS.
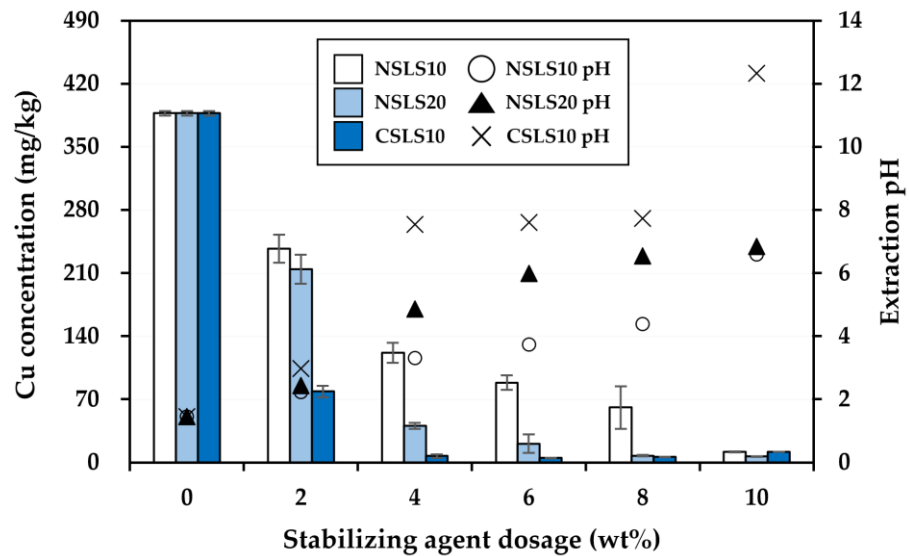

Figure 6. Cu concentrations under -#10 mesh NSLS, -#20 mesh NSLS, and -#10 mesh CSLS treatment (28 days curing; 0.1 N HCl extraction).
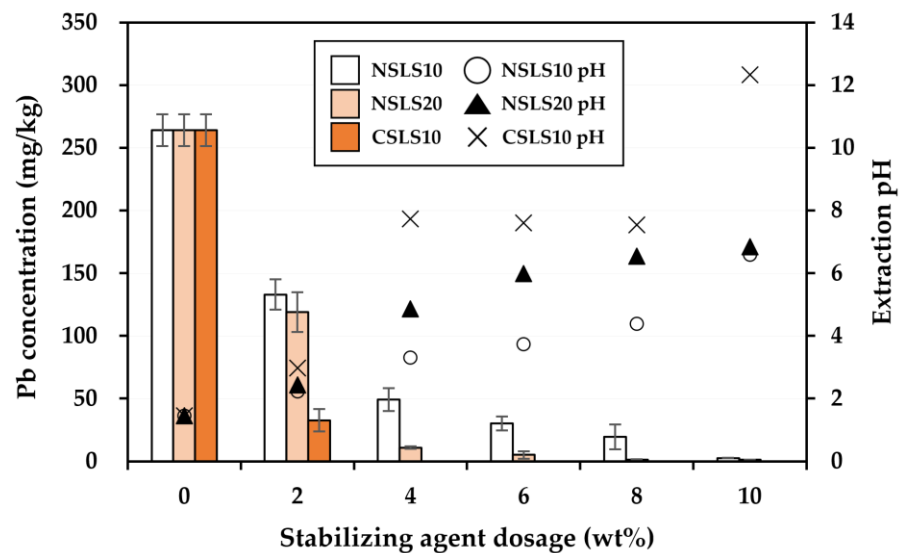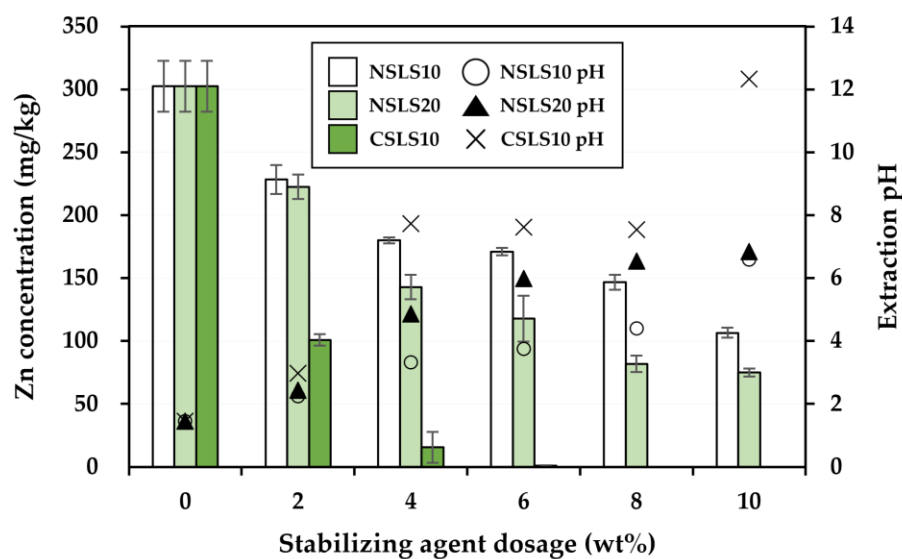

Figure 7. Pb concentrations under -#10 mesh NSLS, -#20 mesh NSLS, and -#10 mesh CSLS treatment (28 days curing; 0.1 N HCl extraction).

When heavy metals in fine soil were stabilized with ASF, the stabilization efficiency was similar to or slightly higher than that obtained using other shells. Compared to the initial control leaching concentrations (Cu: 353.5, Pb: 245.5, and Zn: 319.8 mg/kg), 10 wt% NASF10 treatment reduced the leaching concentrations of copper and zinc to

15.5 and 53.0 mg/kg, respectively. NASF20 treatment further reduced these to 14.9, and 48.1 mg/kg, respectively, and the extraction of lead was minimal under 10 wt% NASF treatment (Figures 9–11). In addition, 10 wt% CASF10 treatment exhibited a leaching concentration of 8.1 mg/kg for copper with the extraction of lead and zinc being minimal (Figures 9–11). Overall, a stabilization tendency similar to that from using SLS was observed. However, the leaching concentration of zinc decreased slightly further after ASF treatment (NSLS10: 106.6 mg/kg, NASF10: 53.0 mg/kg, NSLS20: 75.0 mg/kg, and NASF20: 48.1 mg/kg). A comparison of the treatment efficiency of CSLS10 and CASF10 revealed that ASF was more effective than SLS because the leaching concentrations of zinc were 100.9 mg/kg and 20.2 mg/kg based on 2 wt% treatment, respectively (Figure 9). In this regard, Lim et al. [28] reported that minerals, such as zinc phosphate, can be precipitated when heavy metal-contaminated soil is stabilized with natural starfish (NSF). The authors compared the saturation index (SI) after stabilizing heavy metal-contaminated soil with NSF and $CaCO_3$, respectively, and reported SI values for zinc phosphate of 0.523 (NSF) and -61.752 ($CaCO_3$), respectively. SI is the measure of the solution saturation for a specific mineral. It indicates that no mineral is formed if the SI is lower than -1 and tends to precipitate the SI at higher than zero [28]. Therefore, in this study, it is also possible that a higher stabilization efficiency was observed when zinc was stabilized with ASF, which contains more phosphorus than SLS (Table 2), due to the precipitation of minerals, such as zinc phosphate.
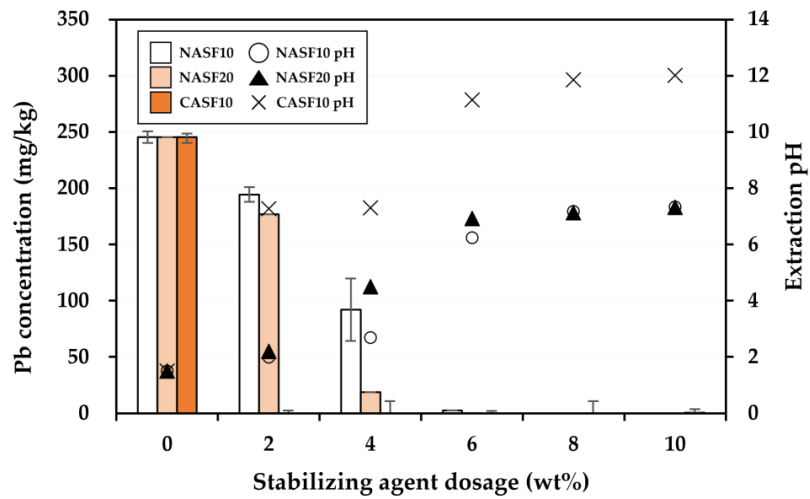

Figure 8. Zn concentrations under -#10 mesh NSLS, -#20 mesh NSLS, and -#10 mesh CSLS treatment (28 days curing; 0.1 N HCl extraction).

After stabilizing the heavy metals with CKS, SLS, and ASF, the leaching concentration of each heavy metal was compared; it was found that the elution of heavy metals increased as the extraction pH decreased, while Zn always showed the largest elution followed by Cu and Pb. This is because each heavy metal is extracted at different pH levels. For example, a previous study [38] performed extraction from the heavy metal-contaminated soil stabilized with cement at various pH levels (4–12) and reported that copper, lead, and zinc were extracted at pH 5 (Pb), 6 (Cu), and 7 (Zn) or less, respectively, and that Zn exhibited the largest elution followed by Cu and Pb at pH 4. In the present study, when heavy metals were stabilized with CKS, SLS, and ASF and then extracted using 0.1 N HCl, the extraction pH varied between 1.3 and 12.3, and Zn also exhibited the largest elution, followed by Cu and Pb, which is consistent with the previous studies (Figures 3–11).
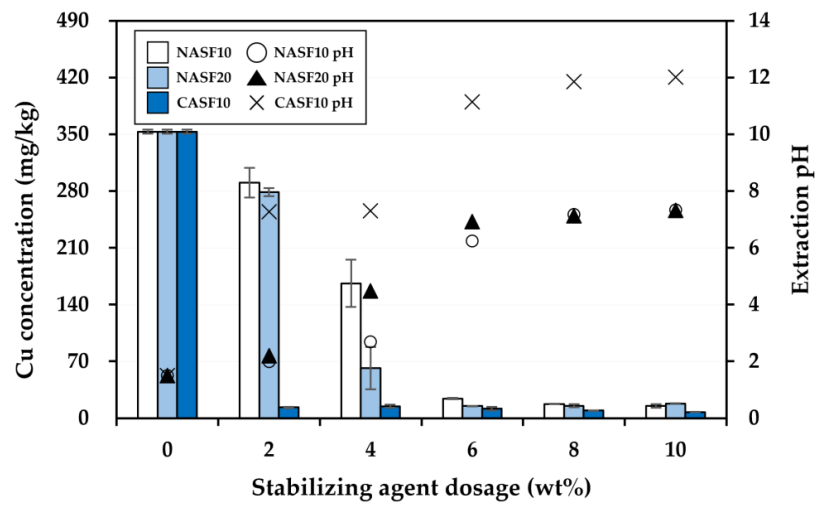
Figure 9. Cu concentrations under -#10 mesh NASF, -#20 mesh NASF, and -#10 mesh CASF treatment (28 days curing; 0.1 N HCl extraction).

Figure 10. Pb concentrations under -#10 mesh NASF, -#20 mesh NASF, and -#10 mesh CASF treatment (28 days curing; 0.1 N HCl extraction).
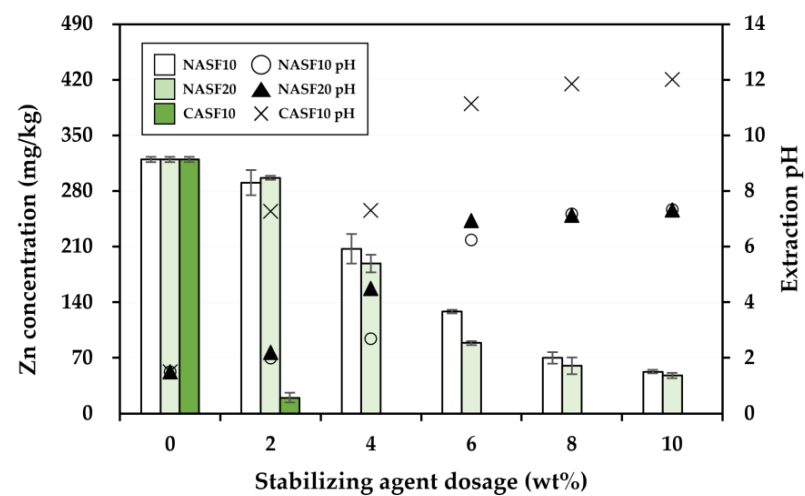

Figure 11. Zn concentrations under -#10 mesh NASF, -#20 mesh NASF, and -#10 mesh CASF treatment (28 days curing; 0.1 N HCl extraction).

A comparison of the stabilization efficiency according to the stabilizing agent processing type showed that the calcined type (-#10 mesh) exhibited the highest efficiency, followed by the natural type (-#20 mesh), and natural type (-#10 mesh). The treatment efficiency was apparently improved as the stabilizing agent particle size decreased due to the increased reactivity of the heavy metals in the soil [22,34]. In addition, the calcination of the stabilizing agents changed the main component from $CaCO_3$ to CaO, and its reaction with water increased the pH by generating one Ca^{2+} ion and two OH^- ions [28]. Accordingly, the pH value of the stabilizing agents, which ranged from 7 to 9 before calcination, exceeded 12 after calcination (Table 2). Therefore, calcined stabilizing agents can decrease the solubility of heavy metals by further elevating the soil pH compared to conventional stabilizing agents and accelerating the precipitation of metal carbonates, oxides, or hydroxides [18,39]. It is also posited that CaO contributed to the stabilization of Cu, Pb, and Zn by increasing the soil pH and forming CAHs and CSHs by releasing Si and Al from the clay under this condition [27,28,30,32,36]. In the present study, it was demonstrated that CASF had the highest stabilization effect on heavy metal-contaminated fine soil, followed by CSLS, CCKS, NASF, NSLS, and NCKS. Similarly, it has been reported that calcined starfish outperformed natural starfish [28,31]. Lim et al. [28] have reported that a significant reduction in TCLP Pb (>91%) and Zn (>93%) concentrations in the contaminated soil was attained using a 2.5 wt%–10 wt% calcined starfish (*Asterina pectinifera*) treatment. Moon et al. [31] also reported that TCLP Pb and Zn leachability was significantly reduced to 93% for Pb and 76% for Zn by the 5 wt% calcined starfish treatment.
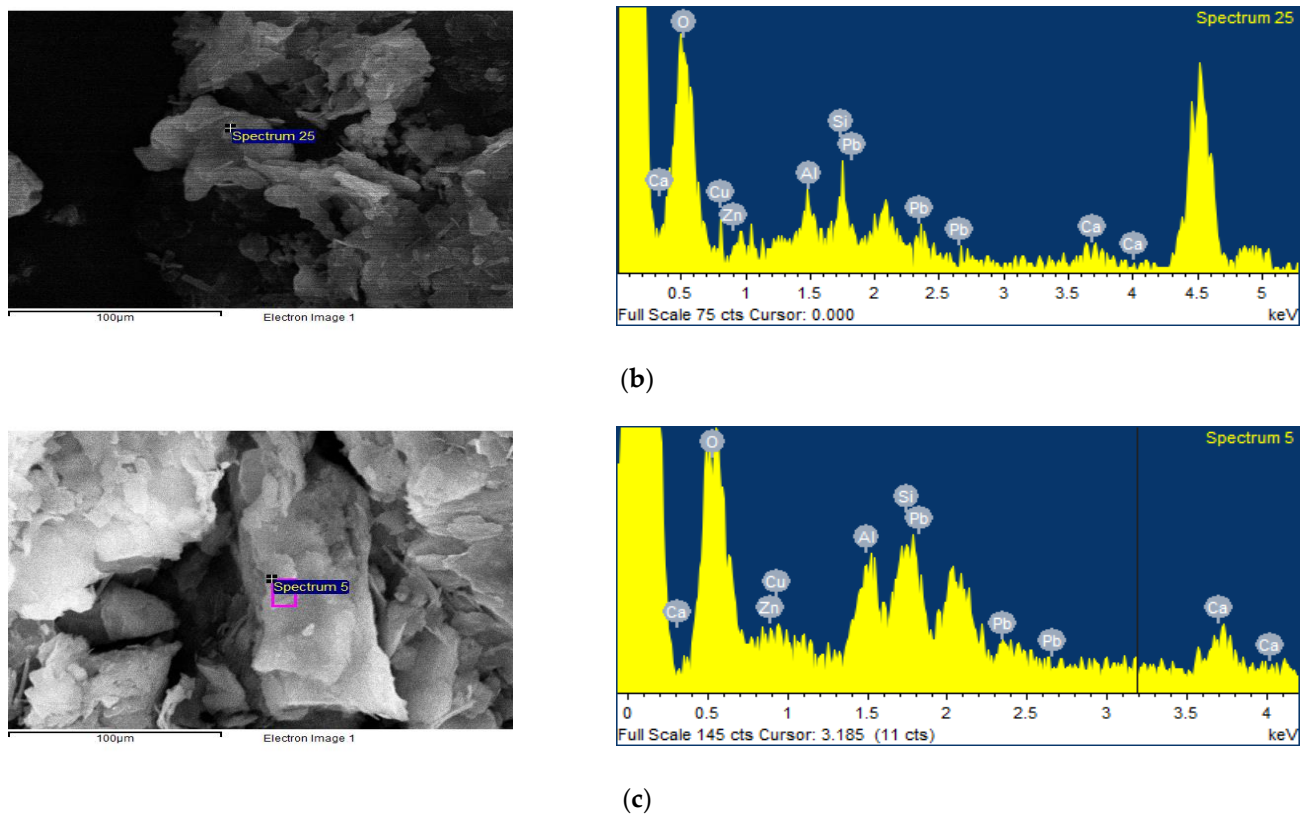
3.3. SEM–EDX Analysis

Figure 12 shows the SEM–EDX analysis results for CCKS10, CSLS10, and CASF10 of 10 wt%, which exhibited the highest stabilization efficiency for Cu, Pb, and Zn. According to the SEM–EDX analysis results, crystals composed of Ca, O, Si, Al, Cu, Pb, and Zn could be found in all samples treated with the stabilizing agents (Figure 12). This could be attributed to the formation of cementitious hydrates (pozzolanic reaction products, i.e., CAHs and CSHs), as reported in previous heavy metal stabilization studies using calcined oyster shells, CKS, or calcined starfish [14,27–32]. Therefore, it can be inferred that Cu, Pb, and Zn were partially encapsulated in pozzolanic reaction products or immobilized through such bonds as Si-O-Pb and Si-O-Zn [31,40,41].

(a)

Figure 12. *Cont.*

(**b**)

(**c**)
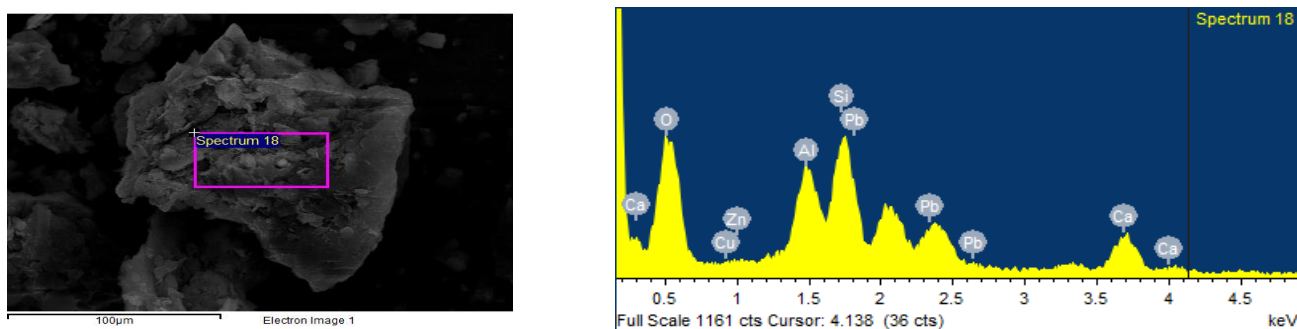
Figure 12. SEM–EDX analysis for Cu, Pb, and Zn in contaminated soil treated with CCKS10 (**a**), CSLS10 (**b**), and CASF10 (**c**) treated sample.

4. Conclusions

In this study, heavy metal-contaminated fine soil generated following high-pressure washing was effectively stabilized using cockle shells (CKS), scallop shells (SLS), and *Asterias amurensis* starfish (ASF). To compare the treatment efficiency according to the stabilizing agent processing method, each material was processed into the natural types of -#10 mesh and -#20 mesh, and the calcined type of -#10 mesh, respectively. Analysis of the leaching concentrations of heavy metals after 28-day stabilization and 0.1 N HCl extraction revealed that the calcined type (-#10) exhibited the highest stabilization efficiency for Cu, Pb, and Zn, followed by the natural type (-#20) and natural type (-#10). Regardless of the stabilizing agent, Pb showed the highest stabilization effect, followed by Cu and Zn. The SEM–EDX analyses results for CCKS, CSLS, and CASF of 10 wt% exhibiting the highest stabilization efficiency, confirmed the generation of pozzolanic products with low solubility, such as calcium aluminum hydrates (CAHs) and calcium silicate hydrates (CSHs). Finally, it can be inferred that the use of CKS, SLS, and ASF, under optimal particle size and calcination conditions, can effectively stabilize heavy metals in fine soil generated after high-pressure soil washing.

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