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Comparison Between the Calcium-Based Stabilizer and Non-Organic Agents on the Stabilization of Contaminated Soil

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Abstract

This study was conducted to investigate the properties of nickel- and copper-contaminated soil and to determine the potential use of calcium stabilizers and inorganic agents as soil improvement methods. The soil was classified as loamy sand (SM) with a low plasticity index (PI = 4%), medium permeability, and high silica content (>33%). X-ray fluorescence (XRF) testing revealed nickel oxide concentrations of 1.5% and copper oxide concentrations of 2.5% in the soil. Nickel and copper contamination based on added nitrate salts was estimated at 1,500 ppm and 2,500 ppm, respectively. X-ray Diffraction (XRD) results showed that quartz and kaolinite were the most abundant, and the contaminants were likely present in an amorphous or surface-adsorbed manner. Unconfined Compressive Strength (UCS) results indicated a significant improvement in compressive strength: from 96 kPa (2% cement, 7 days) to over 12,445 kPa (7% cement, 28 days). The 20% fly ash yielded a strength of 934.5 kPa after 28 days, due to natural pozzolanic reaction and mineral adsorption. Overall, strength improved, and stability was achieved with increased curing time. These results demonstrate that cement and fly ash improved both the mechanical properties and environmental performance of sandy soils contaminated with heavy metals. However, the accelerated strength improvement for cement was significantly greater (over 12,445 kPa) than for fly ash (934.5 kPa, with 20% fly ash) after 28 days of curing. This result suggests that cement-based materials have superior load-bearing performance in applications, but fly ash may be less effective and potentially more environmentally friendly.

Keywords: Contaminated Soil; Heavy Metal Immobilization; Soil Stabilization; Portland Cement; Fly Ash; UCS.

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1. Introduction

Soil is the outermost layer of the Earth's crust, composed of a mixture of minerals and organic matter. Soil is known to be the foundation for building and a habitat for plants. Soil continues to form through the weathering of rocks and the decomposition of living organisms. Soil properties (color, texture, structure, and fertility) vary based on differences in chemical composition and the conditions under which the soil was formed. Heavy metals in soil have become an international environmental issue in recent years, particularly with sites previously considered for industrial activities, oil refineries, and mining [1]. Heavy metals in soil can pose a threat to ecosystem health, groundwater quality, and human health. Sandy soils are naturally highly permeable and therefore are also more susceptible to contaminant infiltration [2]. Soil stabilization methods can be applied to improve the physical and chemical properties of soil, which can improve stability and durability, reduce permeability, improve soil quality, and limit swelling and shrinkage capacity [3]. Stabilizers also contribute to erosion resistance, contributing to resistance to external environmental forces and

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factors [4]. Stabilization with chemical binders is one of the most common methods for improving the physical and chemical properties of soil, including the stabilization of contaminants [5]. Portland cement is a common and widely used stabilizer for soil stabilization, as it can gain strength relatively quickly and can also improve the mechanical performance of contaminated soil through hydration and hardening [6].

However, industrial by-products such as fly ash are frequently used as inorganic materials and are considered pozzolanic materials that affect soil strength and allow for the stabilization of solid contaminants such as heavy metals through adsorption and chemical reaction [7]. However, they affect soil structure and particle size to a lesser extent, but inorganic stabilizers may also affect plant nutrition, moisture retention, and soil pH [8]. Although many studies have been developed on soil stabilization using cement or fly ash, few studies have compared the effects of both in terms of their use in sandy soils contaminated with heavy metals, with different treatment periods and research experiments. The overall objective of this work was to evaluate and compare the effectiveness of calcium-based stabilizers and inorganic stabilizers for soils contaminated and affected by industrial contamination with nickel and copper nitrates. The performance of the treatments was evaluated using unconfined compressive strength (UCS) tests. This is the maximum compressive stress that a material (such as soil or rock) can withstand without lateral support before collapse or cracking. X-ray fluorescence (XRF) is an analytical technique used to determine the elemental composition. X-ray diffraction (XRD) is a technique used to determine the crystalline structure of materials. The scanning electron microscope (SEM) is a device that shows fine details of surface structure and morphology at very high resolution.

The theoretical approach of this study is based on the fundamental mechanisms of soil stabilization and contaminant immobilization. Traditional calcium-based stabilizers, such as cement, enhance soil strength, reduce contaminant mobility, and prevent their infiltration into groundwater, primarily through hydration reactions that produce calcium silicate hydrates (C–S–H) and calcium aluminate hydrates (C–A–H) [9]. These reaction products not only bind soil particles but also precipitate heavy metals by creating an alkaline environment that favors immobilization. These include the highly stable hydroxides and carbonates of nickel and copper used in this research. Inorganic agents, such as fly ash, act as pozzolans, consuming calcium hydroxide and forming additional C–S–H phases, while simultaneously contributing to the production of alumina and silica, which participate in the bonding process between soil particles [10]. These agents enhance the unconfined compressive strength (UCS) and reduce the leachability of heavy metals. Based on this theoretical framework, the current study evaluates and compares the efficiency of conventional calcium-based stabilizers and alternative inorganic stabilizers in remediating contaminated sandy soil.

The remainder of this paper is organized as follows: Section II describes the materials used, the experimental methodology, and the study area, including soil contamination, stabilizer preparation, and testing procedures. The third section presents the results of the tests used, the first of which is the physical and chemical properties of the soil. It also presents the use of X-ray fluorescence (XRF) before and after the soil was contaminated industrially with nickel and copper nitrates, as well as X-ray diffraction (XRD), scanning electron microscopy (SEM), and unconfined compressive strength (UCS). Finally, the fourth section is a comprehensive discussion of the results of the microscopic characterization of the structure based on X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), and unconfined compressive strength (UCS).

2. Materials and Methods

2.1. Study Area

Soil samples were taken in this study from the vicinity of the Dora Refinery, located in the Dora area south of Baghdad, at a depth of approximately one to two meters. The soil surrounding the Dora Refinery contained high concentrations of heavy metals released as a result of combustion within the refinery and its emission into the air, as well as uncontrolled and hazardous materials produced there. Figure 1 illustrates the areas covered by the study.

Nickel (Ni) and copper (Cu) were not chosen because they are the main heavy metal pollutants in the Dora area near the Dora refinery. Recent studies conducted around the Dora oil refinery in Baghdad have shown elevated levels of nickel and copper, which can be found in soil, wastewater, and ambient air released through combustion processes. Since nickel is commonly associated with oil refining processes and copper is associated with corrosion of metal equipment, they are considered environmentally hazardous pollutants due to their persistence, potential for bioaccumulation, and toxic effects on microorganisms and plants. Therefore, they were chosen as the main pollutants in this study to evaluate the effectiveness of stabilization in contaminated soils.

For example, measurable concentrations of nickel and copper were detected in the refinery's industrial wastewater and nearby sediments, while [11] reported that these two metals exceeded permissible limits in the ambient air near the refinery area. Although preliminary EDS analysis of the natural soil used in this study did not show significant traces of nickel or copper, indicating that the base soil was initially free of contamination, these metals were intentionally introduced to induce industrial soil contamination and to stabilize the stabilizers used to evaluate their effectiveness under controlled contamination conditions.

Figure 1. Location of the study area: Baghdad, Iraq, and the Dora Refinery site

2.2. Soil Collection and Preparation

Soil weighing approximately 40 kg was collected at depths of 1–2 m. The soil was excavated using a Hitachi (Zaxi 200) hydraulic excavator, Japan (2014), with a maximum excavation depth of 7–10 m. Impurities and decomposed organic matter were removed by sifting the soil through a 2 mm sieve. Samples weighing 40 kg were air-dried and ground with a pestle to a fineness of less than 75 microns. The soil samples were then chemically and physically analyzed to evaluate the soil structure and composition. When the soil sample was taken from the site, it was slightly moist, and roots, rocks, and sandy aggregate constituted most of the debris.

2.3. Contamination Procedures

After sifting and drying approximately 20 kg of soil, an artificial soil contamination procedure was conducted. After the sifted soil was mixed with a specific amount of nickel and copper nitrate (1500 and 2500 mg/kg, respectively), predetermined concentrations of Ni^{2+} and Cu^{2+} were selected based on reported contamination levels in soils affected by oil refineries. Aqueous solutions of the salts were prepared and gradually mixed with the dry soil, adding distilled water, which may be sufficient to add the required organic matter concentration to achieve a homogeneous distribution. After the soil was sprayed with the mixed nickel and copper solution, the soil was placed in a tightly sealed bucket and left for seven days at room temperature to monitor the physical and chemical changes in the contaminated soil.

2.4. Stabilizing Agents

Two different stabilizing agents were used in this study: a conventional calcium-based stabilizer (ordinary Portland cement, OPC) and an inorganic pozzolanic material (Class F fly ash).

Ordinary Portland Cement (OPC): Commercially available ordinary Portland cement (OPC) was used as a calcium-rich binder. This cement is suitable for all soil types and can be used in any type, especially when the organic matter content is less than 2%. Cement is a binder containing a significant amount of calcium and undergoes hydration reactions in the presence of water. The cement reacts with water to produce calcium silicate hydrate (C-S-H) and calcium hydroxide ($Ca(OH)_2$). These reactions produce products that help stabilize heavy metals, such as nickel (Ni), copper (Cu), cadmium, lead, zinc, and other heavy metals [12]. Cement contains a high concentration of calcium oxide (CaO) and silicon dioxide (SiO_2), which contribute to the formation of hydration products such as calcium silicate hydrate (C–S–H) and calcium aluminate hydrate (C–A–H).

Fly ash: Class F fly ash, extracted as a byproduct of a thermal power plant, has been used as an inorganic stabilizer. Fly ash can be pozzolanic, where its particles combine during combustion to form an amorphous, glassy structure.

This produces gels of C–S–H and similar compounds in the presence of calcium hydroxide and moisture, with significant amounts of silica (SiO_2) and alumina (Al_2O_3), along with smaller amounts of Fe_2O_3 and CaO, indicating its pozzolanic nature.

For soil stabilization experiments, different cement and fly ash ratios (based on soil dry weight) were selected to evaluate their effects on strength development, pH adjustment, and contaminant stabilization. The selected ratios were based on previous studies and optimized for sandy soil conditions. All stabilizing agents were stored in sealed containers under dry conditions to prevent moisture ingress and loss of reactivity before being mixed with the contaminated soil [13, 14].

2.5. Sample Preparation and Treatment

After thoroughly mixing the contaminated soil, prepared in Section 2.3, with the selected stabilizing agents (cement and fly ash) in predetermined proportions, the stabilizer ratios were selected as percentages of the dry weight of the soil. (2, 5, and 7)% Portland cement and (10, 15, and 20)% fly ash were selected to evaluate the effect of the stabilizing agents on soil performance. The required amount of stabilizer was mixed dry with the contaminated soil until homogeneity was achieved. Distilled water was then added at the predetermined optimum moisture content (OMC), obtained from standard Proctor compaction tests, to facilitate compaction and hydration. The soil, stabilizer, and water mixture was kneaded by hand, then mechanically mixed for 15 minutes to ensure uniform distribution of the stabilizers. Cylindrical specimens with dimensions of 38 mm in diameter and 76 mm in height were then prepared for mechanical testing, according to ASTM D2166 recommendations for unconfined compressive strength (UCS) testing. Each specimen was compressed in three layers inside a mold, then removed using a hydraulic jack and wrapped in nylon wraps to prevent moisture loss and maintain its physical and chemical properties at room temperature during the curing periods (7, 14, and 28 days) to allow sufficient time for the reactions to occur [15].

2.6. Analytical Methods

To assess the physical, chemical, and mineralogical properties of contaminated and stabilized soil, a series of analytical techniques was used:

X-ray Fluorescence (XRF): XRF spectroscopy was used to determine the chemical composition of elements, including the presence of heavy metals (nickel and copper) and their major oxides, present in natural soil. For this analysis, 8 grams of soil were mixed with 2 grams of boric acid, which acted as a binder to mechanically stabilize the particles. The mixture was placed under a pressure of 2-5 tons (about 30 s). The XRF instrument operated at a voltage of 60 kV and a current of 50 mA [16], and the completed sample was transferred to an XRF sampler for analysis at the Environment and Water Management Laboratory of the Ministry of Science and Technology. This technique enabled the accurate quantitative determination of major/minor elements.

X-ray Diffraction (XRD): X-ray diffraction analysis was performed to study the mineral composition of natural soil. This analysis is suitable for identifying mineral types (quartzite, kaolinite, illite, and montmorillonite). The oven-dried samples (105°C) were ground to a fine powder, and approximately 10 grams of soil were placed in an XRD holder made of non-radioactive plastic. This analysis enabled the identification of crystalline phases, including quartz, kaolinite, illite, and montmorillonite. The samples were oven-dried (105°C), and a sample weighing approximately 10 grams was taken and placed in an XRD holder made of plastic or a special non-radioactive metal to determine the mineral composition [16].

Scanning Electron Microscope (SEM): The scanning electron microscope (SEM) was used to examine the surface morphology and microscopic changes in natural untreated soils. The surface texture of soil particles (smooth, rough, or cracked) was visualized. The sample was placed at a depth of approximately 1 gram from the dried soil, and sufficient pressure was applied to reveal the soil's textural classification. SEM images allowed observation of particle morphology and the development of cementitious products (such as C-S-H and C-A-H gels) within the soil [17].

Unconfined Compressive Strength (UCS): The unconfined compressive strength (UCS) test was performed the to evaluate the mechanical performance of contaminated soil before and after stabilization. Cylindrical specimens were prepared, placed for specified periods (7, 14, and 28 days), and subjected to axial stresses until failure. The UCS values provided a measure of the improved compressive strength associated with the addition of cement and fly ash.

The flowchart of the research methodology that was used to achieve the study's aims is shown in Figure 2.

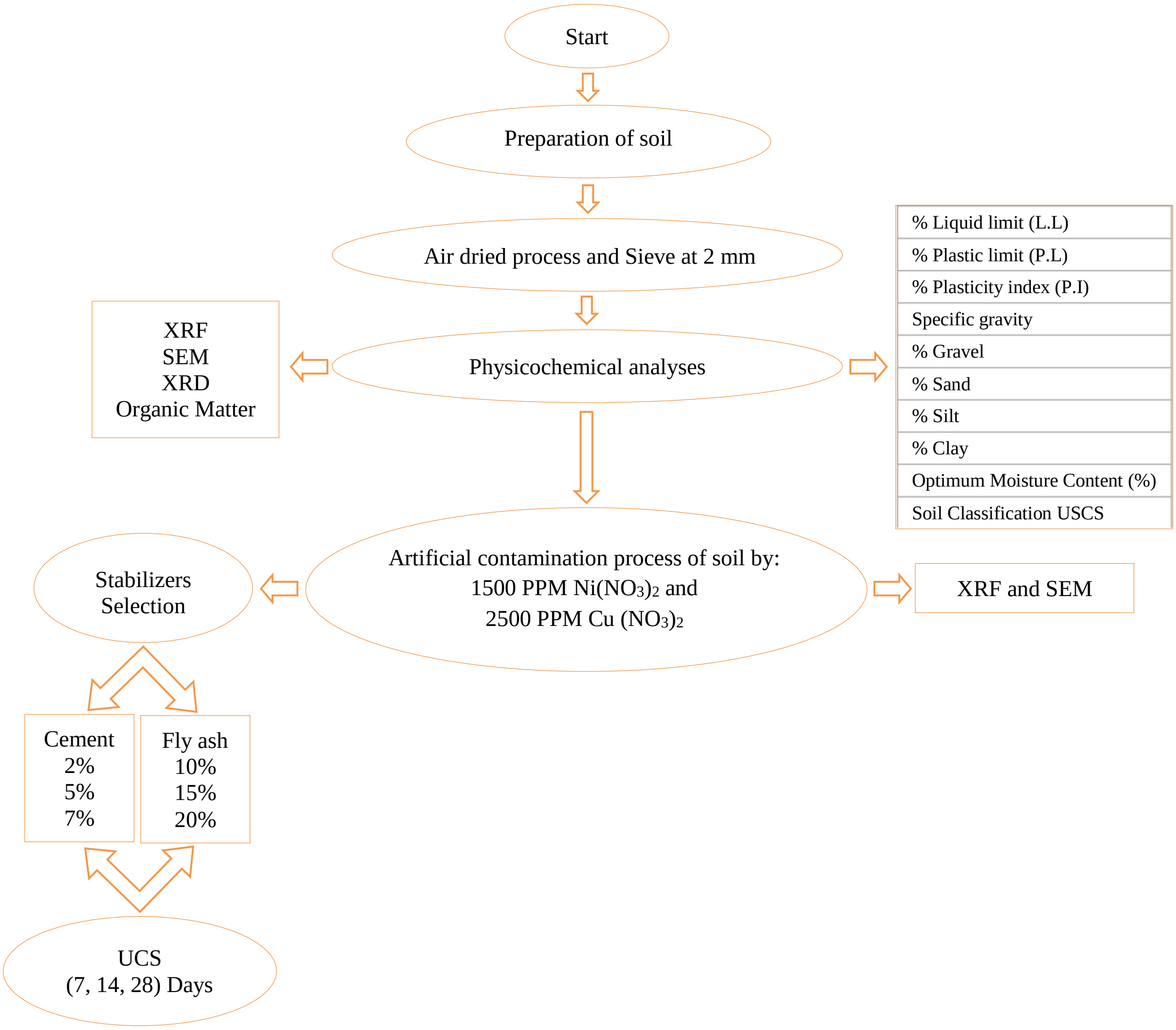

Figure 2. Flow chart of the experimental design

3. Results and Discussion

3.1. Physical and Chemical Properties of Soil

The geotechnical analysis performed on the soil sample, shown in Table 1, indicated important properties for assessing the soil behavior under environmental stress (contaminated areas), which exhibited moderate plasticity and a sandy-loamy (SM) texture. Geotechnical tests showed a liquid limit (LL) of 22% and a plastic limit (PL) of 18%, providing a plasticity index (PI) value of 4%. LL and PL indicate a soil with low plasticity and a slightly plastic group or class as defined by the Unified Soil Classification System (USCS). The PI value of the soil is consistent with the behavior of a sandy loam (SM) soil, with sufficient clay content to alter the plasticity. Consider the results of Abhishek et al. [18]. Who analyzed an urban clay soil in Hillah, Iraq? The reported LL values ranged from 21% to 70%, and the PI values varied by 33% or 43%. The present results indicate a less cohesive and therefore more granular soil. Based on the above results, it is reasonable to conclude that the soil type at this site may have been influenced by natural sedimentation, human influences, and industrial activity. The specific gravity (Gs) of 2.69 is somewhat characteristic of mineral soils rich in quartz and silicates [19], indicated that the average Gs of the uncontaminated sedimentary soil in central Iraq was 2.65, which also indicates that it may be composed of heavy metal oxides (this was also confirmed by XRF, which showed elevated concentrations of (Fe_2O_3 and TiO_2).

The results also showed that the grain size distribution was consistent with a sandy composition, containing 43% sand, 41% silt, and 16% clay, meaning that it would also be classified as a loamy sand (SM) based on the USCS system. The absence of any gravel content was also important to confirm the integrity of the sample homogeneity, and there is a possibility that the composition is an eroded siliceous material. These results are also consistent with Salih et al. [20]. Who reported on soils in oil-affected areas in Basra, and identified SM and ML as indicated by Regassa et al. [21]. This means that the permeability is medium and the cohesion is low, allowing contaminants, including heavy metals, to move vertically downwards and into the groundwater through the Soil. The results indicated that the optimum moisture content

(OMC) of 11% had a moderate water-holding capacity, and the OMC was generally average for sandy loam soils. Furthermore, the recorded OMC ratios (13–18%) were lower for clay-rich soils, which reported some clay in the soil periphery near the Tigris floodplain [22]. This suggests that the soils in this study would dry out quickly and therefore have a greater potential to require more frequent wetting in remediation treatments, such as vegetation treatment or soil washing.

Table 1. summarizes the general characteristics of the soil

Properties	Values
% Liquid limit (L.L)	22
% Plastic limit (P.L)	18
% Plasticity index (P.I)	4
Specific gravity	2.69
% Gravel	0
% Sand	43
% Silt	41
% Clay	16
Optimum moisture content (%)	11
Soil classification USCS	Silty sand

3.2. X-Ray Fluorescence (XRF)

XRF analysis of a natural soil sample before industrial contamination. Figure 3 shows the elements found in this analysis before treatment. Concentrations of silicon dioxide (SiO_2) exceeded 33%. This indicates a sandy soil, as sandy or quartz soils contain quartz. The sample contained moderate amounts of alumina (Al_2O_3) and iron oxide (Fe_2O_3), and low amounts of calcium oxide (CaO), indicating that the sample represents a limited range of clays and minerals.

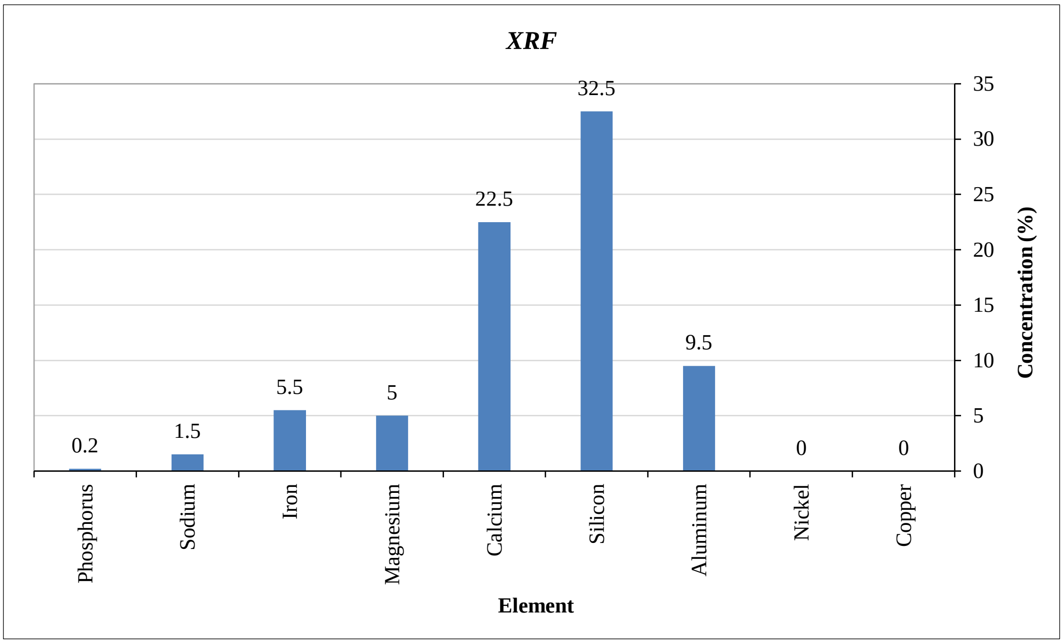

Figure 3. XRF analysis of uncontaminated soil

Evidence suggests that these elements are still capable of migrating depending on the conditions without the need for transport, and therefore, the need for stabilization and remediation techniques to limit potential movement into the environment was justified. These results were likely considered similar to those of Majeed et al. [23]. For heavy metals observed in soils from other areas of Iraq, sandy soils consistently contained a higher percentage of silica than other soils [24]. The study also demonstrated the effectiveness of XRF technology in clearly defining soil structure and its accuracy in detecting subtle differences between different soil conditions, even when contaminating elements were present at low concentrations.

After soil contamination with nickel and copper nitrates, the values in the XRF test varied, and the results are shown in Figure 4.

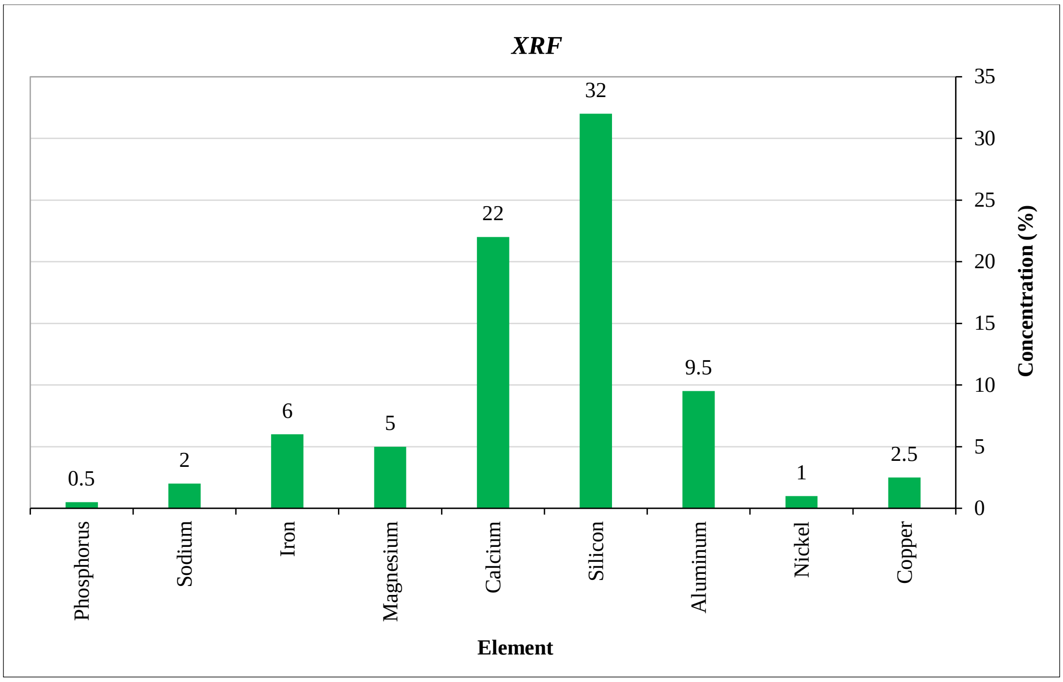

Figure 4. XRF analysis of contaminated soil with nickel and copper nitrates

X-ray fluorescence (XRF) analysis conducted after intentionally contaminating sandy soil with nickel and copper nitrate revealed the presence of 1.5 nickel oxide and 2.5 copper oxide. While the required contamination levels based on added nitrate salts were 1,500 ppm nickel and 2,500 ppm copper, this corresponds to the oxide values measured using XRF, which were significantly lower for the oxide forms in the study. The discrepancy is likely due to adsorption onto soil particles, losses from sample processing, and conversion of nitrate to oxide or other forms not detected by XRF. However, the reported values remained within the range of observed values collected from contaminated soils near contaminated industrial and mining sites [25]. Comparative research indicates that exceptional soil contamination with nickel and copper (particularly from electroplating, smelting, and solid waste disposal) generally produces soil concentrations of 100–400 ppm for nickel and 300–700 ppm for copper [26]. Therefore, the current data are consistent with these concentrations and represent an important tool for evaluating stabilization approaches under these realistic contamination conditions. Heavy metals (nickel and copper) in soil generally represent a significant risk from an environmental engineering perspective for several reasons, including toxicity, persistence, and leaching to groundwater. Heavy metals can affect microbial activity, human health, and plant uptake if left unchecked [27].

Therefore, the first step in any soil remediation technique is to measure heavy metal concentrations via XRF. XRF data demonstrate that nickel and copper are primarily present in the oxide form. Research has shown that such minerals can be stabilized in cement and, in some cases, in fly ash by encapsulation in hydration products such as calcium silicate hydrate (C–S–H), and chemical substitution reactions in which the metal ions are stabilized in the mineral phase [28]. The binding of the metal ions follows pozzolanic reactions resulting from the silica and alumina content of a fly ash sample. It should be noted that pozzolanic reactions occur under alkaline conditions—pH $\geq$ 10—to precipitate metal hydroxides and carbonates [29]. Additionally, the low absolute errors observed in the report by Risoluti et al. [27] included contaminant levels (300 ppm nickel and 600 ppm copper). Results of using a cementitious soil stabilizer with fly ash showed a reduction in residual heavy metal leaching by over 80% and an improvement in the unconfined compressive strength test after 28 days (although the extent of the improvement is unknown). For this purpose, it is concluded that the levels of nickel oxide and copper oxide measured in this case fall within the operational range required for the effectiveness of the proposed method for dual stabilization of heavy metals.

3.3. X-Ray Diffraction (XRD)

We then examined the contaminated soil using X-ray diffraction (XRD) without adding any stabilizers. The goal was to determine the crystal structure and natural minerals present in the sample, and to determine whether mineral phases, such as nickel and copper, were present due to heavy metal contamination. Figure 5 shows the X-ray diffraction pattern of the contaminated sandy loam soil before stabilization, to determine its crystal structure.

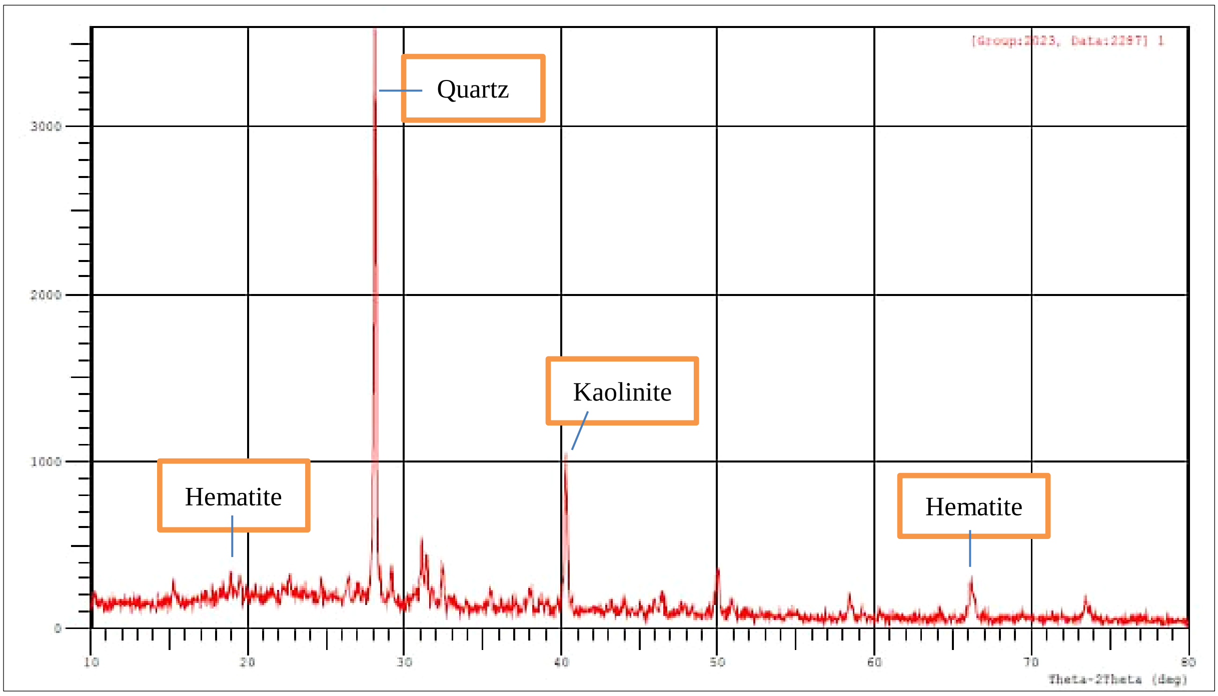

Figure 5. XRD uncontaminated soil

Quartz peaks (26.6°) were prominent, while feldspar and kaolinite peaks were less pronounced, with higher peak heights, while hematite was found at a lower peak. The absence of nickel/copper crystalline phases suggests that they are likely amorphous or adsorbed to mineral particles. Overall, the XRD results indicated the presence of several silicate minerals, primarily quartz (SiO_2), followed by feldspar and kaolinite, respectively. In summary, these minerals indicate a sandy-clay soil with equal contributions from a large amount of chemically neutral, inactive minerals (such as quartz). Several weak hematite (Fe_2O_3) peaks were also found, indicating the presence of iron in its natural oxidized state. These peaks occur in the soil as a result of surface geochemistry. X-ray diffraction (XRD) before stabilization did not show any new mineral formations associated with chemical reactions, and this was confirmed by Genua et al. [30]. It indicated the presence of metal contaminants in the form of amorphous phases or adsorbents on the surfaces of metal particles. This is also consistent with Fu et al. [31]. Who confirmed that XRD does not clearly show the presence of heavy metal contaminants unless the contaminants are present in a stable crystalline phase where they can be resolved into an intrinsic crystal.

3.4. Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) images of untreated natural soil, shown in Figure 6, show the morphology of surface features indicative of an unimproved and possibly contaminated soil, with loose, cohesive particles, high porosity, and characteristic porosity. This is indicative of a variety of soils whose overall characteristics tend toward poor cohesion and a degree of openness that allows for the movement of contaminants such as nickel and copper ions. The illustrations show that the particles are thin and there are no mineral deposits covering the surfaces. This lack of mineral accumulations indicates the absence of stabilizing chemical interactions or physical bonds that would otherwise contribute to enhanced soil structural stability, as explained by Goodarzi & Zandi [32].

Figure 6-a shows that the soil particles have sharp, irregular angles, increasing their likelihood of sliding under load or high moisture conditions, indicating a high susceptibility to disintegration and fragmentation. The images in Figure 6-b also show some mineral contaminants deposited in irregular patches across the surface of the particles, highlighting that significant adsorption of these contaminants is limited and that effective stabilization is lacking at this stage. Some fine particles were observed between the larger particles, which may have been suspended contaminants or possibly some previous surface contact incorporation, but not enough to produce a comprehensive structure as described in Yan et al. [33] and Fischer et al [34]. There appears to be no evidence of surface coatings or crystalline formations, meaning that the materials would need to be reasonably effective stabilizing agents that properly interact with the contaminants and fill the voids between the particles. These results certainly suggest that methods could be explored to improve the structural cohesion of soils by adding materials that help reduce porosity.

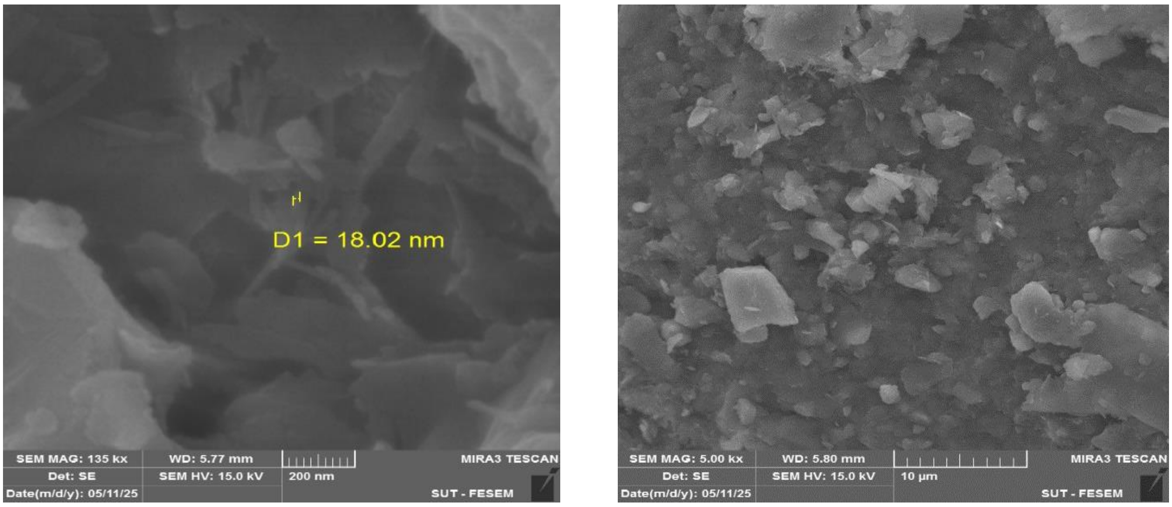

Figure 6. Scanning Electron Microscopy (SEM): (a) soil microstructure at the Nano level before treatment; (b) surface morphology consisting of particles of varying shapes and sizes distributed against a relatively smooth background

3.5. Unconfined Compressive Strength (UCS)

The study was executed to enhance the mechanical properties of sandy soil affected by heavy metals (nickel and copper), which was stabilized using two agents, which were a calcium-based stabilizer and a non-organic agent. The contaminated soil was treated with different percentages of stabilizers, and the unconfined compressive strength (UCS) was evaluated after 7, 14, and 28 days of cure for the performance assessment of these two treatments.

3.5.1. Effect of Heavy Metal Content with Cement on UCS of Stabilized Soil

In this section, Figure 7 shows the UCS value for a soil sample industrially contaminated with Ni^{+2} and Cu^{+2} ions. The unconfined compressive strength of this sample was measured before adding any stabilizer (UCS = 45 kPa). This parameter was focused on for comparison with the presence of heavy metals and improving soil stabilization with cement. Figure 7 shows the strength ratios (2%, 5%, and 7%) for soil samples treated with cement and contaminated with heavy metals at concentrations of 1500 and 2500 mg/kg of (Ni^{+2} and Cu^{+2}) at treatment times of 7, 14, and 28 days. Figure 7 also shows that the increase in UCS was associated with the cement content. An increase in the compressive strength of the contaminated soil can also be observed with increasing cement content for all samples used. The UCS values for samples containing 2% cement with HM alone were (96, 185.2, 4480.2) kPa, while the unconfined compressive strength recorded at 5% cement at the same curing time and conditions was (165, 300, 7806) kPa. The unconfined compressive strength recorded at 7% cement at the same curing time and conditions was (280, 9861, and 12444.9) kPa. The results showed that the 10% cement ratio had a higher UCS value across all curing days, and it was several times higher than the 2% and 5% ratios, especially on day 28 of curing.

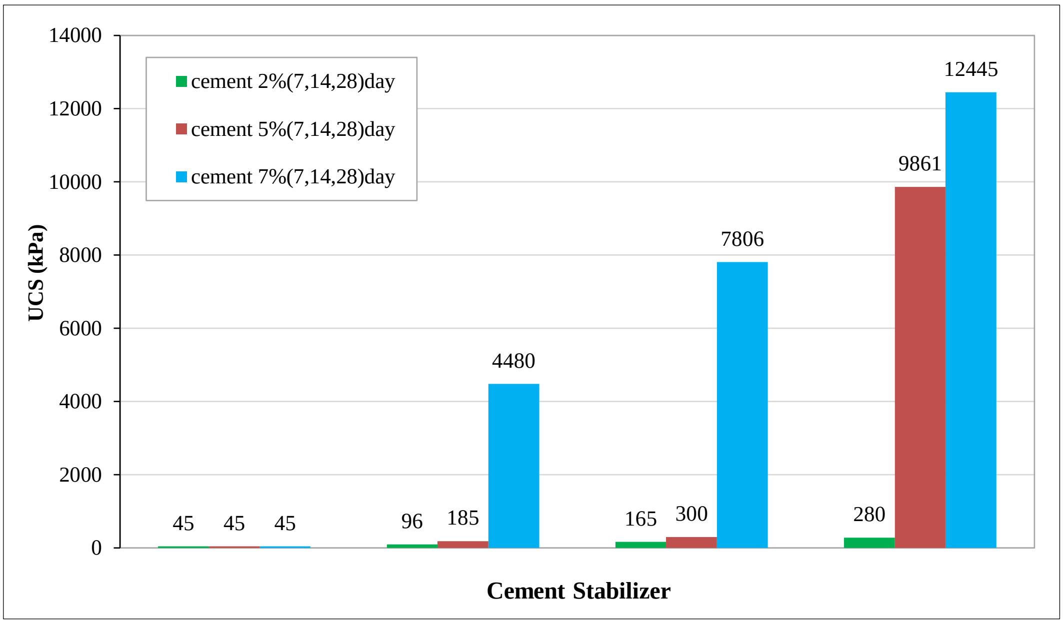

Figure 7. UCS results for contaminated soil mixture with only cement

The increase in strength of sandy soil samples contaminated with heavy metals at all treatment times is due to the addition of cement. Cement releases calcium hydroxide ($Ca(OH)_2$), which dissociates into Ca^{+2} and OH^- ions. The release of OH^- ions increases with the increase in pH, leading to the dissolution of silica and alumina in the industrially contaminated sandy soil particles. These dissolved materials subsequently react with calcium ions to form cementitious byproducts, the most important of which are calcium silicate hydrate (C–S–H) and calcium aluminate hydrate (C–A–H), which are pozzolanic products and are primarily responsible for the significant improvement in the durability and compressive strength of the contaminated soil [35]. The gradual increase in unconfined compressive strength (UCS) of industrially contaminated sandy soil stabilized with cement is also demonstrated, as the pores gradually fill and bind soil particles into a more cohesive structure. The formation of C–S–H and C–A–H bonds is the primary mechanism responsible for the improved durability, along with the stabilization of Ni^{+2} and Cu^{+2} ions in the soil matrix. This bonding effect reduces the mobility of heavy metals by encapsulating them within the hardened cementitious matrix, enhancing mechanical performance and environmental safety.

In addition to pozzolanic reactions, carbonation plays a secondary but important role. Calcium hydroxide released during hydration can react with atmospheric carbon dioxide to form calcium carbonate ($CaCO_3$), a crystalline phase that further contributes to the durability of treated soils. The combination of hydration, pozzolanic reactions, and carbonation explains the increase in UCS with longer treatment periods. In addition, the results of this study showed that higher cement content provides an increased supply of calcium ions, accelerating the scope of pozzolanic activity and enhancing the development of cementitious products. As a result, the compressive strength of the treated samples increased with both treatment time and cement dosage. These results indicate that cement stabilization is an effective approach not only for improving the strength of sandy soils contaminated with heavy metals, but also for achieving significant stabilization of heavy metals through chemical stabilization and physical encapsulation within the cement matrix. Increasing the curing time leads to increased pozzolanic reactions, thus increasing the compressive strength of the treated samples. Cement content plays an important role in compressive strength. It was found that the UCS increased when the cement content increased from 2% to 5% and even to 7%. We can also conclude that a 7% cement content is suitable for stabilizing sandy soils containing heavy minerals, which is consistent with the results of the study [36].

3.6. Effect of Heavy Metal Content with Fly Ash on UCS of Stabilized Soil

Figure 8 shows the results of the unconfined compressive strength of sandy soil industrially contaminated with heavy metals and stabilized with an inorganic substance such as fly ash at different ratios (10%, 15%, and 20%). The sample compacted without the use of a stabilizer showed relatively low strength. When the initial 10% fly ash ratio was added to the industrially contaminated sandy soil for different time periods (7, 14, and 28 days) and compacted with a UCS device, a significant improvement in the compressive strength (UCS) was observed compared to the sample to which no stabilizer was added. The results showed that the UCS values were (210.7, 333.4, 453.4) kPa. These chemical processes produce calcium silicate (C-S-H) and calcium aluminate (C-A-H) hydrates that fill the spaces between sand particles, enhancing cohesion, reducing permeability, and improving load-bearing capacity. This improvement is also attributed to the pozzolanic reaction of the fly ash [37]. These hydration products contribute to the initial development of bonding between soil particles, while stabilizing a portion of the heavy metal ions through adsorption and precipitation mechanisms. When using 15% fly ash, over the same time periods, the UCS values increased even further (390.2, 545.1, 847.9) kPa. This indicates that the additional amount of reactive components enhanced the pozzolanic reactions and generated more cementitious gels [38].

Heavy metal stabilization was also more effective at this level, providing a greater number of reactive sites for ion exchange and bonding. At this stage, the soil matrix became denser, with reduced porosity, which positively impacted overall strength. The highest UCS values were recorded with 20% fly ash (510.5, 661.5, 934.5) for the same conditions and treatment days. At this dosage, the maximum benefit was achieved from pozzolanic activity, as a large amount of hydration products developed and encapsulated both soil particles and contaminant ions. This resulted in the formation of a compact and stable structure that exhibited greater compressive strength. Thus, increased fly ash content was directly correlated with higher UCS values for soils industrially contaminated with 1500 mg/kg nickel nitrate and 2500 mg/kg copper nitrate. The results show that fly ash can significantly improve the UCS of contaminated sandy soils, improving their density and cohesion, while also adsorbing heavy metal ions such as nickel and copper, reducing their mobility and toxicity, which can be achieved even at the highest fly ash content of 20% [39, 40].

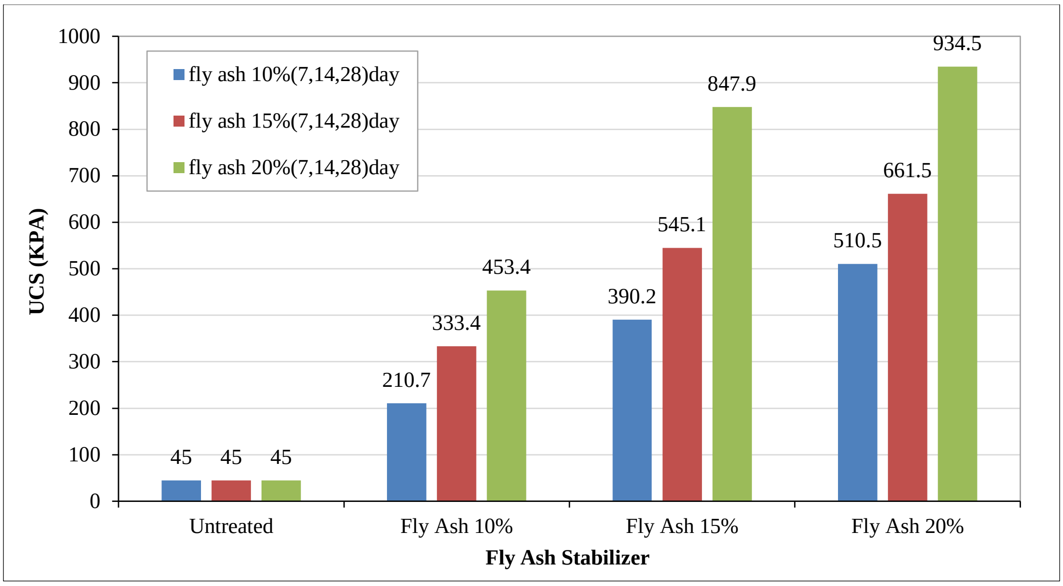

Figure 8. UCS results for contaminated soil mixture with only fly ash

4. Conclusion

The study evaluated the geotechnical and geochemical behaviors of sandy soils that have been contaminated with heavy metals (nickel and copper), and demonstrated the performance of Portland cement and fly ash as stabilizing agents. Preliminary assessments determined the soil to be clayey sand (SM) per USCS classification, with moderate permeability and significant silica content (>33%), making it very conducive to contaminant transportability. Scanning electron microscope (SEM) imaging also showed the soil type to have a loose grain structure and a highly porous condition, indicating minimal structural cohesion and illustrating the need to improve its mechanical properties. In terms of geotechnical improvements, unconfined compressive strength (UCS) testing demonstrated a substantial increase in soil strength with stabilization. Portland cement gained significantly better mechanical performance overall. The UCS values increased substantially with cement ratios and an increase in curing. For example, the UCS value increased from 96 kPa with 2% cement after 7 days of curing to over 12,445 kPa with 7% cement after 28 days. This improvement could be attributed to fast hydration and pozzolanic reactions that generated the calcium silicate hydrate (C-S-H) gel. The C-S-H generated a gel that filled voids among sand particles, thus binding the sand particles together and improving the soil's bearing. Fly ash would also perform adequately as an environmentally friendly substitute.

However, the improvement in strength was significantly less than the strength improvement by cement, finding mostly a UCS value of 934.5 kPa using 20% fly ash after 28 days. The improvement in strength from fly ash is generally attributed to pozzolanic activity and the immobilization of heavy metal ions by the fly ash. Fine fly ash particles can fill voids between sandy soils by densifying the soil and improving cohesion among sand particles. Fly ash will also immobilize heavy metal ions, such as nickel and copper, and thus reduce their mobility and toxicity. This data confirmed that fly ash can be an alternative material for micro-stabilization and environmental remediation through its unique capability to sequester metals. In terms of geochemistry, based on X-ray work done in the pre-treatment analyses, the contaminated soil had 1.5% nickel oxide and 2.5% copper oxide. Although these are lower values than the target amounts originally, informal observations would suggest that these values are consistent with realistic contamination levels. In addition, X-ray diffraction (XRD) analyses of the soil determined that quartz and kaolinite were the dominant minerals in the soil. Also, as there were no recognized crystalline phases of nickel and copper in the XPDI data, this does suggest that there was amorphous contamination or surface-adsorbed contamination that will impact the effectiveness of the stabilizing agents. The findings advocate the use of binder-based stabilization as a possible repair strategy, and the cement and fly ash are also able to stabilize metals by either physically encapsulating metals in their hydration product (physical encapsulation), chemically substituting the metals through a substitution or anion replacement during curing, or precipitating metal hydroxides in an alkaline environment.

5. Declarations

5.1. Author Contributions

Conceptualization, K.A.S., Y.M.F., and D.E.S.; methodology, Y.M.F., K.A.S., and D.E.S.; software, K.A.S., Y.M.F., and D.E.S.; validation, K.A.S. and Y.M.F.; formal analysis, K.A.S., Y.M.F., and D.E.S; investigation, K.A.S. and Y.M.F.; resources, Y.M.F. and D.E.S.; data curation, K.A.S. and Y.M.F.; writing—original draft preparation, Y.M.F., K.A.S., and D.E.S.; writing—review and editing, K.A.S., Y.M.F., and D.E.S.; visualization, K.A.S., Y.M.F., and D.E.S.; supervision, K.A.S. and D.E.S.; project administration, K.A.S. and Y.M.F.; funding acquisition, K.A.S. and Y.M.F. All authors have read and agreed to the published version of the manuscript.

5.2. Data Availability Statement

The data presented in this study are available in the article.

5.3. Funding

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5.5. Conflicts of Interest

The authors declare no conflict of interest.

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