Mechanical Properties and Leaching Characteristics of Geopolymer-Solidified/Stabilized Lead-Contaminated Soil

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Abstract

Ordinary Portland cement (OPC) is widely used in the solidification/stabilization of Pb-contaminated soils. However, many studies have suggested that the high content of Pb would degrade the mechanical properties of OPC-solidified/stabilized soils. This paper presents a new binder, geopolymer fine aggregate (GFA), composed of ground granulated blast furnace slag, fly ash, CaO, and Na2SiO3. For comparison, OPC was used as a conventional binder. Mechanical properties and leaching characteristics are typically used to evaluate the effects of binders on solidified/stabilized soils. Nevertheless, limited information on the mechanical properties and leaching characteristics of the GFA-solidified/stabilized soils is available. This study thus investigated the mechanical properties and leaching characteristics of geopolymer-solidified/stabilized Pb-contaminated soil. Unconfined compressive strength test, permeability test, synthetic precipitation leaching procedure, simplified bioaccessibility extraction, phytoavailability extraction (with diethylene-triamine penta-acetic acid), sequential extraction procedure, mercury intrusion porosimetry, and scanning electron microscopy (SEM) were performed on OPC- and GFA-solidified/stabilized soil. The results showed that the GFA presented a better effect on the mechanical properties and leachability of the solidified/stabilized soils than the OPC-solidified/stabilized soils. The GFA-solidified/stabilized soil displayed considerably lower leachability, bioaccessibility, and phytoavailability of Pb and higher mechanical properties and chemical stability than the OPC counterpart. This study demonstrated that GFA had a better effect than OPC on the solidification/stabilization of Pb-contaminated soils.

1. Introduction

Pb-contaminated soil has become a severe problem in China due to improper waste disposal practices and accidental chemical spills [1]. Pb is hazardous to the environment and human health and degrades the mechanical properties of soils [2]. Bioremediation, washing restoration, and phytoremediation are promising useful remediation methods for Pb-contaminated soils, while solidification/stabilization has been widely used to immobilize Pb-contaminated soil due to its relatively low cost and demonstrated effectiveness over many years [3]. Ordinary Portland cement (OPC) is a binder that has been used in solidified/stabilized Pb-contaminated soils because of its relative convenience and economic advantages [4]. However, OPC production is a high-pollution, high-energy-consuming industry and a large carbon dioxide emitter. As a result, new environment-friendly binders must be urgently developed to substitute for OPC [5]. Many studies have demonstrated that geopolymers are promising options to replace OPC [6]. Geopolymers are mainly composed of inorganic materials (constituting aluminosilicates) and alkali activators. Inorganic materials include calcined kaolin, ground granulated blast furnace slag (GGBS), fly ash (FA), and clay [7–9]. Among these inorganic materials, GGBS and FA are resource conserving and environmentally friendly.
Although many studies have been performed on geopolymer-stabilized/solidified heavy metals, most of them have focused on the interaction of geopolymers and different types of heavy metal solutions [6–8]; few studies are available on geopolymer-stabilized/solidified heavy metal-contaminated soil, and no peer-reviewed literature has methodically investigated the leaching and mechanical properties of heavy metal-contaminated soil treated with GGBS and FA. Recently, the authors have developed a new binder, geopolymer fine aggregate (GFA), which is composed of GGBS, FA, CaO, and Na$_2$SiO$_3$. Mechanical properties and leaching characteristics are widely used to evaluate the effects of binders on solidified/stabilized soils [1, 2, 5]. Limited information on the mechanical properties and leaching characteristics of GFA-solidified/stabilized soils is also available.

This study aimed to investigate the mechanical properties and leaching characteristics of GFA-solidified/stabilized soils. For comparison, OPC was used as a conventional binder. Unconfined compressive strength (UCS) test, permeability test, synthetic precipitation leaching procedure (SPLP), simplified bioaccessibility extraction test (SBET), phytoavailability extraction (with diethylene-triamine penta-acetic acid (DTPA)), and sequential extraction procedure (SEP) were performed on Pb-contaminated soil. Mercury injection porosimetry (MIP) and scanning electron microscopy (SEM) tests were also conducted to reveal the microstructural characteristics of GFA-solidified/stabilized soils.

2. Materials and Methods

2.1. Materials

2.1.1. Preparation of Geopolymers. GFA used in this test was obtained by mixing GGBS, FA, CaO, and Na$_2$SiO$_3$ in a 6 : 12 : 1 : 1 ratio. The particle sizes of GGBS, FA, and CaO were less than 75 μm. GGBS, FA, and CaO used in this study were supplied by Lingshou Rock Mining Products Co., Ltd. Na$_2$SiO$_3$ was supplied by Chinese Medicine Group Chemical Reagent Co., Ltd. OPC was from Huaxin Cement Co., Ltd., China. The chemical properties of materials used in this study are shown in Table 1.

2.1.2. Preparation of Pb-Contaminated Soil. Raw soil used in this study was collected from Qingdao City, China. The physicochemical properties of the raw soil and Pb-contaminated soil are presented in Table 2, which were obtained in accordance with the “Standard for Soil Test Method” of China [10]. Artificially contaminated soil was used in this test due to its high repeatability and homogeneity. Pb-contaminated soils were obtained by mixing a Pb(NO$_3$)$_2$ solution with air-dried clean soil until the Pb(NO$_3$)$_2$ concentration in the soil reached 10000 mg/kg, which represents a universal concentration for Pb-contaminated soil in China [11–13]. Deionized water was then added to the contaminated soil until the water content reached 23.5% (optimum moisture content). The contaminated soil was mixed evenly and braised for 90 days under standard curing conditions (20 ± 2°C, 95% humidity) to allow Pb(NO$_3$)$_2$ and soil to react adequately.

2.1.3. Preparation of Samples. OPC and GFA were added to the Pb-contaminated soil at binder-to-dry soil ratios (C/Sd) of 5%, 10%, and 20%. These materials were mixed in a 10-L Spar-type mixer. The soils were homogenized for 30 min prior to the addition of distilled water. The ratio of addition of water to the binder and dry soil was 1 : 5. The mixtures were compacted in 39.1 mm × 80 mm and 50 mm × 50 mm molds in three layers. The compacted specimens were stored in sealed sample bags and cured under the standard curing conditions (20°C, 95% humidity) for 28 days.

2.2. Test Methods. The unconfined compression test was performed using a universal testing machine following ASTM D4219 [14]. The penetration test was conducted by using a PN3230M flexible-wall permeameter in accordance with ASTM 5084-03 [15]. Leachability of Pb was tested following the US EPA method 1312 [16]. The Pb bioaccessibility test was performed in accordance with the US EPA protocol [17] and British Geological Survey [18]. The Pb phytoavailability test was implemented following the DTPA [19]. The SEP followed the procedures of the modified European Community Bureau of Reference method. This method divided heavy metals into four fractions, namely, exchangeable, reducible, oxidizable, and residual fractions [20]. The changes in pore size of the solidified/stabilized soils were determined by mercury intrusion porosimetry (MIP) using an automatic mercury porosimeter (PoreMaster 33). The changes in microstructures of the solidified/stabilized soils were identified by SEM (Quanta 250). The concentrations of heavy metals in the leachate were determined by inductively coupled plasma mass spectrometry (Agilent 7900).

3. Results and Discussion

3.1. UCS of Solidified/Stabilized Soils. The UCS of solidified/stabilized soils is shown in Figure 1. The UCS significantly increased with the increase in binder dosage. All the UCS of the solidified/stabilized soils was above the 0.35 MPa limit.
defined by the US EPA, regardless of binder types [21]. When the binder dosage increased from 5% to 20%, the UCS of the OPC-solidified/stabilized soil was increased from 0.55 MPa to 3.12 MPa, whereas that of the GFA-solidified/stabilized soil was increased from 0.95 MPa to 4.35 MPa. The increased UCS of pastes with OPC was larger than that with GFA at the same dosage. The increased UCS of the Pb-contaminated soil solidified/stabilized by OPC was attributed to the large production of AFt or C-S-H. For the GFA counterpart, the increased UCS was attributed to the large production of CaO-Al₂O₃-SiO₂-H₂O (C-A-S-H) and Na₂O-CaO-Al₂O₃-SiO₂ (N-A-S-H), which led to a dense coordinated structure of the contaminated soil [22, 23]. Ismail et al. [24] and Aboulayt et al. [9] found that C-A-S-H and N-A-S-H have higher bonding strength than AFt or C-S-H. This result indicated that GFA was more advantageous than OPC in increasing the mechanical strength properties of Pb-contaminated soil.

3.2. Hydraulic Conductivity of Solidified/Stabilized Soils. Figure 2 shows the hydraulic conductivity of the solidified/stabilized soils. The hydraulic conductivity decreased with the increase in binder dosage. When the binder dosage increased from 5% to 20%, the hydraulic conductivity of the OPC-solidified/stabilized soil was decreased from 1.85 × 10⁻⁵ cm/s to 2.13 × 10⁻⁷ cm/s, whereas that of the GFA-solidified/stabilized soil was decreased from 3.31 × 10⁻⁶ cm/s to 8.25 × 10⁻⁸ cm/s. The decreased trend of hydraulic conductivity was mainly due to the development of binder hydration. A large amount of hydration products (such as C-A-S-H and N-A-S-H) formed and gradually filled the soil pores, which caused the reduction in hydraulic conductivity. These results indicated that the GFA-solidified/stabilized soil had lower permeability than the OPC-solidified/stabilized soil. Zhang et al. [25] found that permeability determines the durability of solidified/stabilized soil, and a low permeability significantly increases service time. Compared with OPC-solidified/stabilized soil, the GFA counterpart could maintain higher durability in an eroded environment.

3.3. Leachability of Solidified/Stabilized Soils. The Pb concentration of the solidified/stabilized soils in the SPLP leachate is shown in Figure 3. The Pb concentration decreased with the increase in binder dosage. For the untreated soil, the Pb concentration was approximately 147.8 mg/L, which greatly exceeded the standard for hazardous waste regulatory limit in China [26]. When the binder dosage increased from 5% to 20%, the Pb concentration in the OPC-solidified/stabilized soil was decreased from 66.3 mg/L to 4.7 mg/L, whereas that in the GFA-solidified/stabilized soil was decreased from 16.6 mg/L to 0.09 mg/L. The Pb concentration in the GFA-solidified/stabilized soil with 10% dosage was below the threshold allowed by the standards for hazardous waste regulatory limit in China (<5 mg/L) [26]. The Pb concentration in the OPC-solidified/stabilized soil with 10% dosage was (15.7 mg/L) higher than that in the GFA-solidified/stabilized soil (4.6 mg/L). The Pb concentration in the GFA-solidified/stabilized soil with 20% dosage was below the threshold of China environmental quality standards for surface water of agriculture use (0.1 mg/L) [27]. These results indicated that GFA presented a better effect than OPC in the solidification/stabilization of Pb.

3.4. Bioaccessibility of Solidified/Stabilized Soils. The Pb concentration of the solidified/stabilized soils in the SBET leachate is shown in Figure 4. The Pb concentration

<table>
<thead>
<tr>
<th>Properties</th>
<th>Raw soil</th>
<th>Lead-contaminated soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water content (%)</td>
<td>19.68</td>
<td>23.45</td>
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<tr>
<td>Specific gravity</td>
<td>2.68</td>
<td>2.79</td>
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<tr>
<td>Liquid limit (%)</td>
<td>41.6</td>
<td>39.2</td>
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<tr>
<td>Plastic limit (%)</td>
<td>21.8</td>
<td>20.5</td>
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<tr>
<td>Optimum moisture content (%)</td>
<td>23.5</td>
<td>21.9</td>
</tr>
<tr>
<td>Maximum dry density (g/cm³)</td>
<td>1.72</td>
<td>1.78</td>
</tr>
<tr>
<td>Soil pH</td>
<td>7.56</td>
<td>5.72</td>
</tr>
<tr>
<td>Clay particle fraction (&lt;0.005 mm) (%)</td>
<td>29.3</td>
<td>3.5</td>
</tr>
<tr>
<td>Silt particle fraction (0.005–0.075 mm) (%)</td>
<td>69.4</td>
<td>72.6</td>
</tr>
<tr>
<td>Sand particle fraction (0.075–2 mm) (%)</td>
<td>1.3</td>
<td>23.9</td>
</tr>
<tr>
<td>SiO₂ (%)</td>
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<tr>
<td>Al₂O₃ (%)</td>
<td>18.72</td>
<td>18.74</td>
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<td>Fe₂O₃ (%)</td>
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<tr>
<td>K₂O (%)</td>
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<td>2.13</td>
</tr>
<tr>
<td>Na₂O (%)</td>
<td>0.56</td>
<td>0.57</td>
</tr>
<tr>
<td>CaO (%)</td>
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<tr>
<td>MgO (%)</td>
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<td>1.11</td>
</tr>
<tr>
<td>TiO₂ (%)</td>
<td>0.86</td>
<td>0.87</td>
</tr>
<tr>
<td>PbO (%)</td>
<td>—</td>
<td>0.98</td>
</tr>
<tr>
<td>Loss on ignition (%)</td>
<td>5.12</td>
<td>4.14</td>
</tr>
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</table>

Table 2: Physicochemical properties of soil used in this study.
decreased with the increase in binder dosage. For the untreated soil, the Pb concentration was approximately 97.8 mg/L. When the binder dosage increased from 5% to 20%, the Pb concentration in the OPC-solidified/stabilized soil was decreased from 75.8 mg/L to 35.1 mg/L, whereas that in the GFA-solidified/stabilized soil was decreased from 46.3 mg/L to 4.7 mg/L. These results indicated that the Pb concentration of the solidified/stabilized soils in the SBET leachate was higher than that in the SPLP test. The reason might be that the pH of the leachate in the SPLP test was higher than that in the SBET given the pH-dependent characteristic of Pb. With the same reductant dosage, the leached Pb concentration of the GFA-solidified/stabilized soil in SBET was noticeably lower than that of the OPC-solidified/stabilized soil. This phenomenon indicated that GFA could notably reduce the bioaccessibility risk compared with OPC.

3.5. Phytoavailability of Pb in Solidified/Stabilized Soils. The Pb content of the solidified/stabilized soils in the DTPA leachate is shown in Figure 5. The Pb content decreased with the increase in binder dosage. For the untreated soil, the Pb content was approximately 1786.9 mg/kg. When the binder dosage increased from 5% to 20%, the Pb content of the OPC-solidified/stabilized soil was decreased from 1576.2 mg/kg to 834.7 mg/kg, whereas that of the GFA-solidified/stabilized soil was decreased from 746.4 mg/kg to 94.3 mg/kg. These results indicated that the Pb content of the OPC-solidified/stabilized soils in the DTPA leachate was higher than that of the GFA-solidified/stabilized soils. Evanylo et al. [28] found that the phytoavailability of heavy metals has a significant correlation with the DTPA-extractable content. Therefore, the results confirmed that the phytoavailability of Pb content in the OPC-solidified/stabilized soils was higher than that in the GFA-solidified/stabilized soils. Compared with OPC, the GFA could notably reduce the phytoavailability of Pb in contaminated soils.

3.6. Species Distribution of Pb in Solidified/Stabilized Soils. The speciation distribution of Pb in the solidified/stabilized soils is shown in Figure 6. For the untreated soil, most of the Pb in contaminated soil exhibited exchangeable (70.32%) and reducible (25.04%) fractions. The oxidizable (4.02%) and residual (1.36%) fractions were minimal. The Pb speciation in the solidified/stabilized soils changed significantly. When the binder dosage increased to 20%, the exchangeable and reducible fractions were significantly changed to 38.45% and 55.36%, respectively, for the OPC-solidified/stabilized soil. On the contrary, the oxidizable (4.81%) and residual (1.38%) fractions were changed slightly. For the GFA-solidified/
stabilized soil, the reducible and oxidizable fractions were significantly increased to 45.32% and 37.26%, respectively. The exchangeable fraction was decreased to 15.86%, and the residual fraction was changed slightly (1.56%). These results indicated that the exchangeable fraction of the OPC-solidified/stabilized soil was mainly converted into reducible fraction, and the exchangeable fraction of the GFA-solidified/stabilized soil was mainly converted into reducible and oxidizable fractions. Petrucci et al. [29] and Zimmerman and Weindorf [30] found that species distribution determines the potential leachability of heavy metals in solidified/stabilized soil. Zhang et al. [31] showed that the availability and mobility of heavy metals in soil are related to the contents of exchangeable forms. In the current study, the exchangeable fraction of Pb in the OPC-solidified/stabilized soil had 20% dosage higher than that in the GFA-solidified/stabilized soil (Figure 6). The difference in leachability of Pb of the OPC- and GFA-solidified/stabilized soil could contribute to the difference in the species distribution. Zhang et al. [32] found that the availability of metals in soil follows the order of exchangeable > reducible > oxidizable > residual. This result indicated better chemical stability of Pb in the GFA-solidified/stabilized soil than in the OPC-solidified/stabilized soil. The reason was the formation of insoluble PbSiO$_3$ and PbSiO$_5$ in the GFA-solidified/stabilized soil [33, 34].

3.7. Cumulative Pore Volume of Solidified/Stabilized Soils. The cumulative pore volume of the solidified/stabilized soils is shown in Figure 7. The cumulative pore volume of the OPC-solidified/stabilized soils was higher than that of the GFA-solidified/stabilized soils. Turning points were observed for the cumulative pore volume of the OPC- and GFA-solidified/stabilized soils; 8.2 μm was the turning point of the OPC-solidified/stabilized soils, whereas 5.8 μm was the turning point of the GFA-solidified/stabilized soils. The result corresponded to the principle of the hydraulic conductivity of solidified/stabilized soils; namely, a small pore volume leads to low hydraulic conductivity of solidified/stabilized soils.

3.8. Pore Size Distribution of Solidified/Stabilized Soils. The pore size distribution (PSD) of the solidified/stabilized soils is shown in Figure 8. For the GFA- and OPC-solidified/stabilized soils added with 20% dosage of cement, their PSD displayed a unimodal type. The pore diameter of the OPC-solidified/stabilized soil ranged from 0.0074 μm to 197.6 μm, whereas that of the GFA-solidified/stabilized soil ranged from 0.0074 μm to 197.9 μm. The PSD curve of the OPC-solidified/stabilized soils was located on the right upper side of the PSD curve of the GFA-solidified/stabilized soils. This condition indicated that the pores of the OPC-solidified/stabilized soils were larger than those of the GFA-solidified/stabilized soils. The changes in the PSD curves of the GFA- and OPC-solidified/stabilized soils were attributed to different hydration products in the soils. For the OPC-solidified/stabilized soils, AFt or C-S-H mainly filled pores with a diameter larger than 1 μm [35]. For the GFA-solidified/stabilized soils, C-A-S-H and N-A-S-H mainly filled pores with a diameter larger than 0.1 μm [36].

3.9. SEM Observations of Solidified/Stabilized Soils. The SEM observations of the solidified/stabilized soils are shown in Figure 9. The microstructures of the untreated soil presented a compact fabric, with a large void space among them. As a result, the untreated soil exhibited low UCS and high hydraulic conductivity. The solidified/stabilized soils presented a dense structure and low porosity. The acicular substances and reticulate products in Figure 9(b) represent AFt (ettringite) and C-S-H, respectively. The cube-like substances and large aggregation in Figure 9(c) represent N-A-S-H and C-A-S-H, respectively. Comparison of Figures 9(b) and 9(c) implied that the microstructures of the GFA-solidified/stabilized soils
Figure 7: Cumulative pore volume of the solidified/stabilized soils.

Figure 8: Pore size distribution of the solidified/stabilized soils.

Figure 9: Scanning electron microscope observations of the solidified/stabilized soils. (a) 0. (b) OPC-20%. (c) GFA-20%.
were dense and had low porosity. The mechanical and leaching test results showed that the GFA-solidified/stabilized soils had better leaching and mechanical properties than the OPC-solidified/stabilized soils. This phenomenon could be attributed to (1) the dense microstructures of the GFA-solidified/stabilized soils, (2) the higher bonding strengths of C-A-S-H and N-A-S-H than those of AFt or C-S-H, and (3) the small pore volume and size of the GFA-solidified/stabilized soils.

4. Conclusions

This study investigated the mechanical properties and leaching characteristics of GFA-solidified/stabilized Pb-contaminated soil. For comparison, OPC was used as a conventional binder. The differences in the mechanical properties and leaching characteristics of GFA- and OPC-solidified/stabilized soils were determined through a series of UCS, leachability, bioaccessibility, phytoavailability, species distribution, MIP, and SEM tests. From the test results, we can draw the following conclusions:

1. The mechanical properties of the GFA-solidified/stabilized soils were better than those of the OPC-solidified/stabilized soils. At the same binder content, the UCS values of the GFA-solidified/stabilized soils were larger than those of the OPC counterpart, and the former had lower permeability than the latter.

2. The GFA presented a better effect than the OPC in the solidification/stabilization of Pb. The GFA-solidified/stabilized soil displayed considerably lower leachability, bioaccessibility, and phytoavailability of Pb than the OPC-solidified/stabilized soil at the same binder content. The Pb concentration in the GFA-solidified/stabilized soil with 10% dosage during the SPLP test was below the threshold allowed by the standards for hazardous waste regulatory limit in China (<5 mg/L). The China environmental quality standard for surface water for agriculture use (0.1 mg/L) was achieved when the dosage was 20%.

3. The differences in the mechanical property, leachability, bioaccessibility, and phytoavailability of Pb of the OPC- and GFA-solidified/stabilized soils were attributed to the differences in species distribution, PSD, and microstructures of the solidified/stabilized soil. For the OPC-solidified/stabilized soil, the exchangeable fraction of Pb was mainly converted into reducible fraction. For the GFA-solidified/stabilized soil, the exchangeable fraction of Pb was mainly converted into reducible and oxidizable fractions. Compared with the microstructures of the OPC-solidified/stabilized soils, those of the GFA-solidified/stabilized soils were denser and showed lower porosity.

Data Availability

The data used to support the findings of this study are included within the article.

Disclosure

Yuan-Yuan Li and Ting-Ting Zhang are the co-first authors.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors’ Contributions

Yuan-Yuan Li and Ting-Ting Zhang contributed equally to the work.

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