Research Article

Effect of Ca/Al Ratio on Stabilization/Solidification of Lead-Contaminated Soil by Ettringite

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Ettringite is commonly used for the stabilization/solidification for heavy metal-contaminated soils, and its treatment effect will be influenced by Ca/Al mole ratio. Lead-contaminated soil samples were solidified using ettringite with different Ca/Al mole ratios. The pH value, unconfined compressive strength of solidified samples, and leaching concentration were investigated to understand the influence of Ca/Al mole ratio on properties of ettringite-solidified contaminated soils. The microstructural characteristics of solidified contaminated soils were also explored. The results show that lead leaching concentration decreases dramatically with increasing the content of lime and curing time. Lead concentration drops from 49.89 mg/L to 0.19 mg/L when Ca/Al mole ratio increases from 4:3 to 10:3 at 28 days and from 36.57 mg/L to near 0 mg/L at 90 days. In addition, the unconfined compressive strength of samples drops at first and then increases with the increase of Ca/Al mole ratio. Besides, the pH values of solidified soil and leachate rise with the increase of content of lime. The pH values of solidified soil increase from 9.68 to 11.34, and there is little difference between 28 days and 90 days. However, the pH values of leachate increase from 5.56 to 8.59 at 28 days, and 90-day pH values increase from 5.65 to 9.44. The results of SEM, XRD, and EDS tests also indicate that Ca/Al mole ratio affects the shape of ettringite, the stabilization/solidification effectiveness of contaminated soil, and the pore of solidified soil. When Ca/Al mole ratio equals to 8:3, ettringite content has a substantial increase, and lead leaching concentration is lower than 5 mg/L.

1. Introduction

Heavy metal-contaminated soils have attracted much attention from engineers and environmentalists during the past decades for it may cause significant damages on human health and ecosystem [1]. There are many techniques that can be used to reduce the bad effect of heavy metal-contaminated soils, among which solidification/stabilization is seen as a common way [2–5] with its economic advantage and effectiveness. Solidification/stabilization is to mix contaminated soils with binders to transfer the waste to environmentally acceptable materials for construction [6]. As a type of commonly used binder, the ordinary Portland cement can facilitate the formation of insoluble hydroxide from heavy metal ions through creating an alkaline environment, and its effect of parcel, adsorption, and complexation also promote the solidification process. However, cement production consumes large amounts of nonrenewable resources and energy. For instance, producing 1-ton cement may consume 1.5-ton lime and clay, 113 kg standard coal, and 5000 MJ energy [7]. Moreover, a great deal of pollutants is created in cement production such as CO₂, SO₂, CO, NOₓ, and dust [8].

As part of the cement hydration product, ettringite (3Ca·Al₂O₃·3CaSO₄·32H₂O), named as Aft, can adsorb more external heavy metal ions by replacement and surface electronegativity [9, 10]. When ettringite is used to stabilize/solidify heavy metal ions, ion replacement is related to ion radius [9]. Ion replacement can only occur between ions with similar radius. Not only the typical heavy metal ions Pb²⁺, Cd²⁺, and Cr³⁺ can replace Ca²⁺, Al³⁺, in ettringite, but also SO₄²⁻ can be substituted by oxygen-containing heavy metal anions such as CrO₄²⁻ [11], enabling heavy metal ions to be a part of ettringite crystal, and then the stabilization/solidification of heavy metals can be achieved.

Many studies indicated that the solidification/stabilization of contaminated soils with ettringite may be
affected by the concentration of certain ions. Luz [12] and Peysson [9] prepared two types of cement paste, for which the ratio of phosphogypsum to calcium sulfoaluminate cement was 2:8 and 3:7, respectively, to conduct the stabilization/immobilization tests of heavy metals including Cr$^{6+}$, Cr$^{3+}$, Cd$^{2+}$, Pb$^{2+}$, and Zn$^{2+}$. The leaching test results of solidified cement pastes showed two main findings:

(i) The retentions of Cr$^{3+}$, Cd$^{2+}$, Pb$^{2+}$, and Zn$^{2+}$ reached 99%, regardless of the curing age, the dosage of phosphogypsum, or the concentration of heavy metal ions.

(ii) The retention of Cr$^{6+}$ is closely related to the content of phosphogypsum and the concentration of Cr$^{6+}$.

Wang [13, 14] used ettringite produced by the solution method to stabilize/immobilize Cu$^{2+}$ and Cr ions of different valencies. They reported that the solidifying mechanism and stability of ettringite on Cr$^{6+}$, Cr$^{3+}$, and Cu$^{2+}$ were different. The Cr$^{6+}$ ion squeezed into the interlayer structure of ettringite changed the molecular symmetry and had a great influence on ettringite crystals. When ettringite was in the environment of carbonization, freezing, and thawing, the retention of Cr$^{3+}$ and Cu$^{2+}$ was less affected, but the retention of Cr$^{6+}$ remarkably reduced. Through the stabilization/immobilization tests of cement mortar, Ma [15] pointed that when using sulfoaluminate cement to stabilize/immobilize heavy metal Zn$^{2+}$, the leaching concentration of Zn$^{2+}$ is only 1/4 of the same amount of Portland cement.

The ettringite crystals are mainly produced by the reaction of AlO$_2^-$, Ca$^{2+}$, and SO$_4^{2-}$. The AlO$_2^-$ ions not only determine whether the ettringite can be formed, but also determine its formation rate. The SO$_4^{2-}$ ion has an important influence on stability of ettringite since the ettringite can only exist stably when the mole ratio of SO$_4^{2-}$ and AlO$_2^-$ is greater than 0.42 [16]. The Ca$^{2+}$ is also a significant influencing factor because its content affects the production and stability of ettringite. When the mass ratio of CaO to Al$_2$O$_3$ exceeds 3.5, the ettringite is stable and keeps developing. When the mass ratio is less than 2.0, the ettringite formed at early stage decomposes partially and transforms into monosulfate calcium sulfoaluminate [17].

In order to clarify the effect of Ca/Al mole ratio on the stabilization and immobilization of heavy metal lead by ettringite, this study investigated the physical, mechanical, and leaching performances of solidified soil with different Ca/Al mole ratios. The binder consisted of high-alumina cement, lime, and gypsum and remained the total content of 15% through experiments, and the S/Al mole ratio kept unchanged. Changes of Ca/Al mole ratio were achieved by adjusting the content of lime. By means of scanning electron microscopy (SEM), X-ray diffraction (XRD), and mercury intrusion porosimetry (MIP), this study also investigated the microcosmic mechanism that the Ca/Al mole ratio affects the leaching and mechanical performances of solidification/immobilization of heavy metal-contaminated soil by ettringite. The results revealed that the variation of Ca/Al mole ratio in ettringite has significant influences on its performance when solidifying/stabilizing lead-contaminated soils.

2. Materials and Methods

2.1. Test Material. The basic physical properties of test soil are given in Table 1. Based on Table 1, the soil is named as silty clay with the liquid limit of 57.2% and plastic index of 14.3%. According to the compaction test, the optimum water content of the soil sample was 15.4%. With the reference that the optimum water-cement ratio for hydration of sulfooaluminate cement is 0.6 [18], the water content of soil sample was set as 24%.

The composition of binder is shown in Table 2. The binder was made up of high-alumina cement, lime, and gypsum to study the effect on Ca$^{2+}$ and Al$^{3+}$ ion contents on ettringite production. This series of binder was named ASC in which A, S, and C represent high-alumina cement, gypsum, and lime, respectively. To ensure that the mole ratio of SO$_4^{2-}$ ions to Al$^{3+}$ ions is greater than 0.42 and its effect on results is excluded, the S/Al mole ratio was kept as 2:3, and the lime content was changed. In Table 2, sample number is the mole ratio of Ca/Al.

Table 3 shows the composition of substances in binder measured by X-ray fluorescence (XRF). Based on the content of Al$_2$O$_3$, CaO, and SiO$_2$, it was found that the content of monocalcium aluminate is the largest, accounting for about 75% of the total mass. The calcium silicate and impurities accounted for 20% and 5%, respectively.

2.2. Test Method. Sample preparation. The mass ratio of binder to dry soil was set as 15%, the water content was 24%, and the concentration of lead was 5000 mg/kg. The mould with a diameter of 50 mm and the height of 100 mm was used to prepare samples, and the mass of a sample is 1500 g. After preparation, the samples were put into standard maintaining room with a controlled temperature of 370 ± 10°C. After preparation, the samples were used to prepare standard maintaining room with a temperature of 20 ± 2°C and relative humidity of above 95%.

The unconfined compressive strength tests were conducted for samples maintained to a predetermined age using the CBR-2 load ratio tester, referring to the specification ASTM D4219-02 [19].

According to the solid waste extraction procedure for leaching toxicity-acetic acid buffer solution method (HJ/T 300-2007) [20], this study extracted heavy metal Pb$^{2+}$ from solidified soils, and its concentration was measured using an absorption spectrometer.

The microstructure, pore structure, and mineral composition were analyzed by SEM, XRD, and MIP tests.

3. Results and Discussion

3.1. Temperature. In the ASC series of samples, the sample temperature decreases as the lime addition increases. This shows that the hydration reaction of ASC series binder is smaller than that of cement hydration reaction.

Figure 1(a) shows the fluctuation of temperature with time in the first three days of solidified soil samples and ordinary Portland cement samples with different lime contents. The temperature of samples reached steady states.
within 24 hours. And the temperature of cement sample was higher than that of the ASC series. In the ASC series of samples, the temperature decreased as the lime content increased, which indicated that the hydration of ASC series released less heat than cement.

The temperature changes in the first 12 hours are shown in Figure 1(b). It can be seen from the partial enlarged detail that the sample temperature has reached a steady state in the first 12 hours, and the heat release was mainly concentrated in the first 4 hours. With the increase of lime content, the temperature change of the sample in the first 4 hours decreased sharply. The high temperature at that time was caused by the heat release of the reaction between lime and water, but the temperature difference was within 3 °C. When the samples were mixed, the lime had released plenty of heat. Therefore, the influence of lime on the sample temperature was small and not considered in the subsequent experiments.

### 3.2. Water Content.

The water content of solidified soil samples with different lime contents is shown in Figure 2. The water content of all ettringite-solidified soils reduced with the increase of lime content. The water content slightly decreased at 28 days while reduced from 18% to around 14% at 90 days. It can be concluded that as the lime content and curing time enhanced, the decrease of water content became larger.

The binder was composed of high-alumina cement, gypsum, and lime. The high-alumina cement mainly contained mineral components like calcium monoaluminate and calcium silicate. In the hydration of binder, it took 26 units of water (excluding the crystal water in gypsum) to generate 1 unit of ettringite crystal. Without producing ettringite, hydration of the same binder consumed only 12 units of water, indicating that the water used for producing ettringite was much larger than that used for the hydration of high-alumina cement and lime.

### Table 1: Physical properties of tested soil.

<table>
<thead>
<tr>
<th>Plastic limit (%)</th>
<th>Liquid limit (%)</th>
<th>Optimum water content (%)</th>
<th>Maximum dry density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.9</td>
<td>37.2</td>
<td>15.4</td>
<td>1.938</td>
</tr>
</tbody>
</table>

### Table 2: Composition of binder (unit: %).

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Al:Ca:S mole ratio</th>
<th>High-alumina cement</th>
<th>Lime</th>
<th>Gypsum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca/Al = 4:3</td>
<td>3:4:2</td>
<td>7.5</td>
<td>0</td>
<td>7.5</td>
</tr>
<tr>
<td>Ca/Al = 6:3</td>
<td>3:6:2</td>
<td>6.36</td>
<td>2.28</td>
<td>6.36</td>
</tr>
<tr>
<td>Ca/Al = 8:3</td>
<td>3:8:2</td>
<td>5.6</td>
<td>3.8</td>
<td>5.6</td>
</tr>
<tr>
<td>Ca/Al = 10:3</td>
<td>3:10:2</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

### Table 3: Material composition (unit: %).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>SO₃</th>
<th>Fe₂O₃</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-alumina cement</td>
<td>44.75</td>
<td>8.95</td>
<td>32.16</td>
<td>/</td>
<td>1.86</td>
<td>12.28</td>
</tr>
<tr>
<td>Lime</td>
<td>/</td>
<td>/</td>
<td>99.99</td>
<td>/</td>
<td>/</td>
<td>0.01</td>
</tr>
<tr>
<td>Gypsum</td>
<td>/</td>
<td>/</td>
<td>36.50</td>
<td>52.14</td>
<td>/</td>
<td>11.36</td>
</tr>
</tbody>
</table>

As shown in Figure 2, without producing ettringite, as the lime content increased, the theoretical water content enhanced when the hydration was complete. Figure 2 also presents that the curing time became larger, and water content reduced as the lime content increased, indicating the production increase and long-term stability of ettringite.

Many studies indicated that some changes would appear with the increase of temperature: at 100°C, ettringite will lose a tiny portion of crystal water [21]; at 130°C, the thermal decomposition of gypsum will cause it to lose part of crystal water [22]; at 270°C, the thermal decomposition of hydrated calcium aluminate will cause it to lose a large amount of crystal water [23]; at 400°C, the structure of hydrated...
calcium aluminate will be still stable [24]; at 580°C, calcium hydroxide will decompose into CaO and H$_2$O.

3.3. Solidified Soil Leaching Toxicity. Figure 3 shows the change of the pH of the pore solution and the leachate of the solidified soil when the lime content varied. In terms of Figure 3, with the increase of lime content, the pH of the solidified soil pore solution increased substantially linearly. Apart from that, the curing time had little effect on the pH of the pore solution. As for the pH of the leachate, it also grew with the increase of lime content. When the lime content was low, the pH climbed slowly, but under the condition of high lime content, the pH surged rapidly. Moreover, the pH of the leachate at 90 d was higher than that at the 28 d.

The leaching concentration of solidified heavy metal-contaminated soils with different lime contents is presented in Figure 4. The concentration of heavy metal Pb$^{2+}$ in solidified soil was 5000 mg/L, and the curing time was 28 d and 90 d, respectively. As shown in Figure 4, with the increase of lime content and curing time, the leaching concentration of heavy metals declined. Besides, it should be noticed that the concentration of Pb$^{2+}$ ion leaching of Ca/Al = 10 : 3 solidified soil was much lower than 5 mg/L prescribed in the hazardous waste standard at 28 d, which was 0.1911 mg/L. Furthermore, at 90 d, the concentration of the solidified soil sample with Ca/Al = 8 : 3 was 3.66 mg/L, also lower than 5 mg/L. This is because the formation of ettringite requires a certain amount of Ca$^{2+}$: When the content of calcareous lime increases, the pH of the solidified soil increases, the Ca$^{2+}$ concentration increases, and the amount of ettringite increases, which significantly improves the solidification effect of heavy metals. The ettringite has long-term stability. With the increase of curing time, ettringite is stably present and continuously formed, and the effect of curing/stabilizing the heavy metal is further improved.

3.4. Strength Properties of Solidified Soil. The change of the unconfined compressive strength of heavy metal-contaminated soils stabilized/solidified by ettringite is shown in Figure 5.
It presents that as the lime content increased, the unconfined compressive strength fell first and then rose. When the quantity of lime was small, the development of soil strength mainly resulted from the cementation between soil particles and calcium aluminate produced by the hydration reaction of high-aluminum cement. As the lime content increased, the content of high-aluminum cement declined, and the cementation between calcium aluminate and the soil particles was weakened, but the filling effect of ettringite on the soil pores became stronger, contributing to the growth of strength. Besides, cementation and filling cannot replace each other. When the curing reached 90 days, the unconfined compressive strength was about 2 times that of 28d, which indicated that as the curing time passed by, the hydration reaction of the binder continued, and both the cementation and filling effect kept the trend of increase, benefiting the strength growth of soil samples.

3.5. Analysis of Microscopic Test Results

3.5.1. Analysis of Mercury Injection Test Results. The cumulative pore volume change of solidified soil samples during the 90 days of curing is shown in Figure 6, and the pore distribution density is presented in Figure 7.

As can be seen from Figure 6, with the growth of lime content, the cumulative pore volume of the sample first increased and then declined, followed by Ca/Al = 8:3, 10:3, 6:3, and 4:3 in a descending order. The cumulative pore volume curve of the samples was slightly different. For Ca/Al = 4:3 and 6:3, the curves were comparatively flat, and the cumulative pore volume rose rapidly below 1 μm. For Ca/Al = 8:3 and 10:3, the curves eased after a dramatic increase when the aperture was 10 μm. As for the aperture that was less than 0.01 μm, the curve was gentle.

Figure 7 indicates that when the amount of lime was small, the pore size of the sample was mainly distributed between 0.1 μm and 1 μm; when the amount of lime was large, that is, Ca/Al = 8:3 and 10:3, the sample pore size distribution focused on 0.1 μm–1 μm and 5 μm–10 μm, respectively. The peaks of the pore distribution density curves of the samples with Ca/Al = 6:3 and 8:3 were more to the left than the samples with Ca/Al = 4:3 and 10:3, and the peak value of the samples with Ca/Al = 6:3 and 8:3 was slightly higher.

Obviously, when Ca/Al = 6:3, the filling effect of the binder on the sample exerted the best because the pore distribution density reached a peak around the 0.1 μm, and the cumulative pore volume was the smallest. When Ca/Al = 8:3, there were two peaks of the curve: the low peak value still stayed around 0.1 μm, but marginally decreased...
compared with the one at Ca/Al = 6:3 and the high pore peak value appeared at 5 μm–10 μm and reached 0.30 mL/g, manifesting that the ettringite generated by the binder expanded the soil sample and developed cracks. When Ca/Al = 10:3, the peak of the low-peak value fell and shifted to around 0.5 μm and the high-peak value continued to rise to about 0.325 mL/g at the range of 5 μm to 10 μm, indicating that the expansion of ettringite became more obvious. To conclude, with the growth of lime content, the amount of ettringite increased, and the impact on the pore volume and the pore distribution density solidified soil became greater.

3.5.2. Analysis of SEM Experiment Results. From Figure 8, it can be seen that as the content of lime increased, the amount of ettringite increased gradually with the growth of lime content. In this process, the distribution of ettringite altered from suspension in space to adhere to the surface of solid particles. When Ca/Al = 4:3, the hydration products of the binder were mainly hydrated calcium aluminate, and there was a very small amount of ettringite, which was nearly an even dispersion; when Ca/Al = 6:3, the ettringite was in an elongated column shape. Meanwhile, calcium aluminate hydrate interacted with ettringite and evenly filled pores; when Ca/Al = 8:3, the amount of the calcium aluminate hydrate content greatly reduced, but the ettringite production increased a lot, and the ettringite began to aggregate to the surface of particles; when Ca/Al = 10:3, the ettringite was the main hydration products of the binder, which grew on the surface of soil particles.

According to Figure 8 combined with the data of mercury injection experiment, after the increase of ettringite production and the shift of the generation place of the ettringite, a large number of pores with the sizes of 5 μm to 10 μm were produced in the solidified soil samples. The increase in porosity would decrease the strength of the soil samples; however, the increase in the content of ettringite would improve the strength of the solidified soil samples due to the filling effect of pores. Therefore, controlling the ettringite content and the generation place is of great significance for the strength of the solidified soil sample.

3.5.3. Analysis of XRD Experimental Results. XRD test was conducted on solidified soil samples with different lime contents. The test pattern is shown in Figure 9. The ordinate refers to d, which is a dimensionless quantity. The abscissa is the diffraction angle 2θ, and there is a corresponding relationship between d and 2θ.

When the characteristic peak d value of ettringite reached 5.61, it can be easily discriminated and was not disturbed by other mineral peaks [25]. When Ca/Al = 4:3 or 6:3, only a small amount of ettringite peaks could be analyzed. When Ca/Al = 8:3 or 10:3, the peak at d = 5.61 was obvious, and both the height and the number of other peaks increased. It shows that the content of ettringite is positively relevant to the lime content.
4. Conclusions

This study used the binders with different proportions of high-alumina cement, lime, and gypsum to immobilize lead-contaminated soils. The effect of mole ratios of Ca/Al on the physical performance and leaching characteristic of immobilized soil was investigated. The mineral composition and microstructure of immobilized soil was also studied. The following conclusions can be drawn:

(1) With the Ca/Al mole ratio increasing from 4:3 to 10:3, the leaching concentration of lead reduced from 49.89 mg/L to 0.19 mg/L at 28 days and from 36.57 mg/L to 0 mg/L at 90 days. The pore fluid pH value in solidified soil at 28 days was not significantly different from that at 90 days, increasing from 9.68 to 11.34. The pH value of leachate increased from 5.56 to 8.59 at 28 days and increased from 5.56 to 9.44 at 90 days. When the Ca/Al mole ratio was 8:3, the leaching concentration of lead at 90 days was 3.66 mg/L, which meets the standard of 5 mg/L for hazardous waste. It is concluded that the Ca/Al mole ratio of the binder used for stabilizing/solidifying heavy metals based on ettringite should be greater than 8:3.

(2) According to results from the microtests, with the increase of Ca/Al mole ratio, the ettringite content in solidified soil increased and crystals moved from inner space to surface of soil particles.

(3) As the Ca/Al mole ratio increased, the unconfined compressive strength of solidified soil decreased firstly and then increased. The unconfined compressive strength at 90 days was 2 times that at 28 days. The strength of solidified soil mainly depended on the filling effect of ettringite and the cementation of hydrated calcium aluminate. Thus, the increase of lime content weakened the cementation and enhanced the filling effect.

(4) As the curing time and Ca/Al mole ration increases, the water content reduces, indicating that the promotion of lime content is beneficial to ettringite formation and its long-term stability which will increase with time elapse.

(5) A large amount of heat was released by the reaction between lime with water, and the exotherm was mainly concentrated in the first 4 hours. The sample temperature has reached a steady state until the first 12 hours, and the temperature difference was controlled within 3°C. Therefore, the influence of lime on sample temperature was small and not considered.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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