Effects of pH and Fineness of Phosphogypsum on Mechanical Performance of Cement–Phosphogypsum-Stabilized Soil and Classification for Road-Used Phosphogypsum

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Abstract: This article investigates the effects of phosphogypsum (PG) pH and particle fineness on the mechanical properties of cement–PG-stabilized soil. Using solutions of calcium hydroxide (Ca(OH)2) and sulfate (H2SO4) to adjust pH value of PG from 2 to 8. The key pore size used to characterize PG fineness was determined to be 200 µm based on the Grey relational analysis (GRA), and the fineness of PG was controlled from 12.31% to 56.32% by grinding different time. Cement–PG cementitious materials (CPCM) and cement–PG-stabilized soil with different mixture ratios were formed at an optimum moisture content; following this, the unconfined compressive strength and California bearing ratio values of the samples were tested. Results show that the increased pH or the decreased fineness leads to continuous increases in the unconfined compressive strength of CPCM and cement-PG stabilized soil as well as the CBR value of cement–PG-stabilized soil. However, once PG pH value exceeded 5 or fineness was less than 20%, the mechanical properties of cement–PG-stabilized soil remained stable. A classification standard for road usage PG was established based on the analyses regarding cement-PG stabilized soil’s mechanical properties, which has great significance of selecting or disposing road-used PG.

Keywords: road engineering; phosphogypsum; grey relation analysis; fineness; subgrade soil

1. Introduction

To ensure sufficient subgrade strength and bearing capacity of pavement, original subgrade soils with poor performance are sometimes subjected to certain technical treatments during road construction. Chemical stabilization is a very common disposal measure of technical treatments, it involves the modification of soil properties to improve engineering performance. Ghazi M found that cement can improve soil properties of Pb-contaminated soil and using JET device can consume testing time and conserving energy. Researchers also proposed formulas to mathematically predict the influence of different stabilizer on the mechanistic erodibility parameters [1,2]. The two most commonly-used chemical stabilization methods are lime stabilization and cement stabilization.

However, the process of production of lime has great impact on environment, the emitted particles and gas produced during the process will seriously pollute the atmosphere. Additionally, cement production, which leads to various forms of pollution, has increased rapidly over the past decade, and deposition practices can seriously affect ambient aerosol levels [3,4]. Therefore, considering environmental benefits, it is imperative to find alternatives for traditional inorganic
Phosphogypsum (PG), an industrial byproduct of the phosphoric acid production, mainly comprises calcium sulfate dihydrate (CaSO$_4$$\cdot$2H$_2$O), though it also contains impurities such as soluble phosphorus, eutectic phosphorus, insoluble phosphorus, fluoride, and organic compounds because of the imperfection of the technology. If impurities such as P$_2$O$_5$ and F$^-$ are not removed when PG is used with cement, they will affect the setting time and strength of Portland cement. Thus, to use PG as a setting retardant, purification, drying, and calcination processes must be implemented [5–12]. PG can also cause harmful radon emissions, however, most chemical companies have ignored that, and use open-air stacking methods to dispose of the PG. This causes PG cannot be effectively used and to pollute soil and groundwater and might expose people working around the site, or living nearby, to contaminants [13–15]. Thus, the problem of stacking PG is an urgent matter to solve. PG can be used to produce fly ash-lime-PG bricks instead of traditional burned clay bricks for use as building material. Fly ash-lime-PG bricks are lighter and have sufficient strength and durability for typical use [16]. This indicates that PG can be used in building materials, but if PG can also be widely used in road construction engineering, the problems of stacking PG and contamination of cement and lime can be simultaneously solved.

The utilization of PG in highway engineering has been extensively studied. When mixed with cement and class-C fly ash, PG can stabilize expansive or non-expansive soils. Using PG for construction, rather than disposing it, is favorable for both economic and environmental reasons when considering the high cost of cement [17]. Strydom [18] demonstrated that PG can successfully replace natural gypsum as a retardant for both ordinary Portland cement and fly ash Portland cement; however, minor impurities in PG affect early strength of cement. Kumar [19] found that a mixture of lime, fly ash, and PG can be applied to the road based on unconfined compressive strength and unconsolidated undrained triaxial tests. It has been confirmed that self-leveling underlayments can be produced using heated PG as the main binder, but the handling time is short, requiring the use of retarders [20]. Additionally, a lime, fly ash, and PG mixture can be used to improve behavior of problematic soils based on an index experiment of unconfined compressive strength, indirect tensile strength, and California bearing rate [21]. Another study confirmed that steel slag-fly ash-PG solidified material can be used for a roadbed [22]. The use of cement-stabilized PG has been recently studied, and it has been found that PG can be used in soil stabilization when stabilized with class-C fly ash and cement [23,24].

These above researches investigated utilization of PG in road engineering, but the properties of PG obtained from different sources might be very different, led to great impact on performances of PG mixtures. Additionally, not only sources of PG can affect PG’s properties, temperature also can seriously affects properties of PG, with thermally treated PG being able to improve the hydraulic properties of Portland slag cement [25,26]. Thus, it is vital to establish or implement the standard of PG with different properties in road engineering. To comprehensively facilitate PG application in road engineering, it is necessary to comprehensively study the relation between PG’s properties and performances of PG stabilized soil. Furthermore, considering the effect of different pH values and fineness of PG on the properties of cement-PG-stabilized soil, which has great significance in the selection or disposal of PG in practical engineering. This study confirms that PG which is an industrial waste of the phosphoric acid production can be used in subgrade to stabilize soil with cement based on the mechanical analysis. Thus, the environmental problem caused by PG can be resolved, and the resource can be recycled to improve the properties of subgrade soil. And the research is also helpful to establish or supplement a standard for PG used in road, considering that this standard is barely given in the current specification.

2. Materials and Methods

2.1. Materials

In this study, PG was obtained from Xi’an city, Shaanxi Province, China. The main component of the PG used was calcium sulfate dehydrate, and its chemical composition is shown in Table 1.
The cement type used was 42.5-grade ordinary Portland cement, which aligns with the guidelines in Test Methods of Cement and Concrete for Highway Engineering [27]. The test results of the cement’s technical properties are presented in Table 2. Loess is yellow powdery soil with columnar formed in dry climate, it was obtained from a local field in Xi’an, and its basic physical and chemical properties, based on the requirements of JTG E40-2007 [28], are shown in Tables 3 and 4. \( W_L \) is liquid limit that refers to the limit moisture content between the plastic state and the fluid state of the cohesive soil, i.e., the upper limit moisture content of the cohesive soil in the plastic state; the moisture content of the soil is too high and the soil can even flow like a liquid when the moisture content of the soil is larger than the liquid limit. \( W_P \) is plastic limit that refers to the limit moisture content between the plastic state and the semi-solid state of the cohesive soil, i.e., the lower limit moisture content of the cohesive soil in the plastic state; the moisture content of the soil is greatly low, and the soil changes from the plastic state to the semi-solid state and loses its plasticity when the moisture content of the soil is less than the plastic limit. The meaning of \( I_P \) is as follows: The plasticity index is an important index characterizing the mechanical and deformation properties of the soil; the value of plasticity index is equal to the difference between liquid limit and plastic limit, i.e., \( I_P = W_L - W_P \).

Table 1. Phosphogypsum chemical properties.

| Constituents          | CaSO\(_4\)-2H\(_2\)O | SO\(_3\) | SiO\(_2\) | Al\(_2\)O\(_3\) | Fe\(_2\)O\(_3\) | P\(_2\)O\(_5\) | F\(^-\) | MgO | Others |
|-----------------------|----------------------|----------|-----------|-----------------|-----------------|---------------|-------|------|--------|
| Mass (%)              | 63.35                | 32.1     | 0.72      | 0.11            | 0.085           | 2.35          | 0.05  | 0.02 | 1.20   |

Table 2. Test results of the technical properties of cement.

| Properties          | Fineness (%) | Stability (mm) | Compressive Strength (MPa) | Flexural Strength (MPa) | Setting Time (min) |
|---------------------|--------------|----------------|----------------------------|-------------------------|--------------------|
|                     |              |                | 3d | 28d | 3d | 28d | Initial | Final |
| Requirements        | ≤10.0        | <5             | ≥17 | ≥42.5 | ≥3.5 | ≥6.5 | ≥240   | ≤390  |
| Results             | 2.5          | 3.8            | 19.2 | 51.4 | 5.4 | 8.6 | 263    | 376   |

Table 3. Physical properties of loess.

| Natural Moisture Content (%) | Liquid Limit \( W_L \) (%) | Water Limit \( W_P \) (%) | Plasticity Index \( I_P \) (%) | Optimum Moisture Content (%) | Maximum Dry Density (g/cm\(^3\)) |
|-----------------------------|-----------------------------|---------------------------|-------------------------------|-----------------------------|----------------------------------|
| 7.62                        | 24.5                        | 18.5                      | 6.0                           | 16.3                        | 1.66                             |

Table 4. Chemical properties of loess.

| Constituents | SiO\(_2\) | CaO | Na\(_2\)O | Al\(_2\)O\(_3\) | Fe\(_2\)O\(_3\) | K\(_2\)O | MgO | Others |
|--------------|-----------|-----|----------|-----------------|-----------------|---------|------|--------|
| Mass (%)     | 61.72     | 8.15| 2.31     | 8.93            | 2.48            | 2.81    | 4.13 | 9.47   |

2.2. Methods

2.2.1. The Definition of PG pH and Fineness

PG that derived from different sources has significant differences in its pH value. To study the effect of pH on cement–PG-stabilized materials, it is vital to define pH value of PG. This is accomplished by mixing PG and water in a 1:10 mass ratio, stirring uniformly, and then letting the mixture stand for 10 min before testing. PG pH refers to the pH value of the supernatant liquid of solution. To explore the pH value’s effect on the strength of cement–PG-stabilized materials, Ca(OH)\(_2\) and H\(_2\)SO\(_4\) were used to adjust the PG solution’s basicity and acidity. After adjusting the pH values, different pH-value PG solutions were dried in an oven at 40 °C until the moisture evaporated, then PG with different pH value are prepared and available for follow-up test.
Fineness refers to the size of particle diameter. There are two common methods to characterize the material’s fineness: The specific surface area method and the use of residue of certain size of a mesh. Because of its complicated testing process, the specific surface area method is limited in practical experiments. The second method used relatively more widely because it is easier to conduct and effectively reflects the surface area of material particles. Thus, this paper used this method to determine the fineness of PG. Note that when using the method, it is significant to confirm the key sieve pore size, which can be determined from the results of Grey relational analysis (GRA).

2.2.2. Grey Relational Analysis

The basic principle of GRA is to consider a microscopic or macroscopic approach between different factors to analyze or determine the degree of influence between each influence factor. The calculation progress of GRA is as follows [29]:

1. Set reference sequence \( \{Y_0(k)\} \) and comparison sequences \( \{Y_i(k)\} \).

2. Average \( \{Y_i(k)\} \) and \( \{Y_0(k)\} \) according to Equation (1), signed as average sequences \( \{X_i(k)\} \).

\[
X_i(k) = \frac{nY_i(k)}{\sum_{k=1}^{n} Y_i(k)}
\]  

(1)

3. Sequences formed by absolute differences between \( \{X_0(k)\} \) and \( \{X_i(k)\} \) are signed as \( \{\Delta_i(k)\} \), \( \Delta_i(k) = |X_0(k) - X_i(k)| \). The correlation coefficient sequence \( \{\xi_i(k)\} \) can be calculated using Equation (2), where \( \Delta_{\text{min}} \) indicates the minimum element of sequences \( \{\Delta_i(k)\} \) and \( \Delta_{\text{max}} \) indicates the maximum element of sequences \( \{\Delta_i(k)\} \). The distinguishing coefficient \( \rho \) in the formula is generally set as 0.5, and thus, \( \rho \) was assigned a value of 0.5 in this paper.

\[
\xi_i(k) = [\Delta_{\text{min}} + \rho \Delta_{\text{max}}] / [\Delta_i(k) + \rho \Delta_{\text{max}}]
\] 

(2)

4. The Grey correlation degree \( \gamma_i \) is expressed as:

\[
\gamma_i = \frac{\sum_{k=1}^{n} \xi_i(k)}{n}
\]  

(3)

5. Because the data were subjected to absolute value processing when calculating the sequences \( \Delta_i(k) \), relational polarity of the Grey correlation degree is difficult to confirm. Thus, relational polarity is determined using Equations (4) and (5). When \( \text{sgn}(Q_i/Q_k) \) equals \( \text{sgn}(Q_0/Q_k) \), the relational polarity is positive. For the opposite, relational polarity is negative.

\[
Q_i = \sum_{k=1}^{n} kX_i(k) - \sum_{k=1}^{n} Y_i(k) \cdot \sum_{k=1}^{n} \frac{k}{n}
\]  

(4)

\[
Q_k = \sum_{k=1}^{n} k^2 - \sum_{k=1}^{n} \frac{k}{n}
\]  

(5)

2.2.3. Unconfined Compressive Strength

Cementitious material and stabilized soil were used to test the unconfined compressive strength (UCS) based on JTG E51-2009 [30]. Specimens were formed in cylindrical shape with dimensions of 50 mm diameter \( \times \) 50 mm height. The loading rate was maintained at 1 mm/min, and the values of failure load (P) and sectional area (A) were documented to calculate the UCS.
2.2.4. California Bearing Ratio

The California bearing ratio (CBR) values of cement-stabilized soil were obtained by determining JTG E40-2007 [28]. The specimen was soaked in water for four days and four nights, after allowing the specimen to stand and drain for 15 min, it was put in the pavement material strength tester (Beijing Haiwei Traffic Instrument Co. LTD, Beijing, China) and loaded at a rate of 1–1.25 mm/min, and the pressure \( p \) (kPa) and penetration \( l \) (mm) values were documented. The CBR value was thus calculated based on the \( p-l \) curve and Equation (6). \( P \) is the pressure value corresponding to the \( l_0 \) (\( l_0 = 2.5 \) mm).

\[
CBR = \frac{P}{7000} \times 100, \tag{6}
\]

2.2.5. Mix Proportions

To study the effects of pH and fineness on cement–PG soil stabilization, the pH value was set to 2–8 using the above methods, and the grinding time of the PG was set at 0, 5, 10, 15, 20, and 25 min to gain different fineness. Three mix proportions of cementitious material and stabilized soil were designed to be tested by considering the precision of the results. It is favorable to understand the basic mechanical properties of PG with different pH value or fineness. The mix compositions of cementitious material and stabilized soil with mix numbers are given in Table 5. CPCM refers to cement-PG cementitious material, and it is formed by PG, cement and water. The results of unconfined compressive strength test or CBR test of CPCM can directly reflect the mechanical properties of cement and PG. The comparison of CPCM and cement-PG-stabilized soil indicates that soil is added into the cement-PG-stabilized soil. Cement-PG-stabilized soil means that cement, PG, water and soil are mixed in a certain proportion.

Table 5. Mix compositions and mix numbers of cementitious material and cement-stabilized soil. PG: Phosphogypsum; CPCM: Cement–PG cementitious materials.

| Mixture Type          | Compositions          | Number |
|-----------------------|-----------------------|--------|
| CPCM                  | Cement: PG = 1:1.5    | M1     |
|                       | Cement: PG = 1:2      | M2     |
|                       | Cement: PG = 1:2.5    | M3     |
|                       | 4% cement + 8% PG     | M4     |
|                       | 5% cement + 10% PG    | M5     |
|                       | 6% cement + 12% PG    | M6     |
| Cement–PG stabilized soil | 4% cement + 8% PG | M4     |
|                       | 5% cement + 10% PG    | M5     |
|                       | 6% cement + 12% PG    | M6     |

3. Results

3.1. Grey Relational Analysis

Taking a cement: PG = 1:2 group CPCM as an example to describe the GRA calculation process, PG was ground for \( k \) min \((k = 1, 2, 3, 4, \text{ and } 5, \) corresponding to grinding times of 5, 10, 15, 20, and 25 min), then cured specimens of cementitious material in a humidity chamber at 20 ± 2 °C and 95% humidity until tested. The elements of the reference sequence \( \{Y_0(k)\} \) comprise seven days of unconfined compressive strength values of the cementitious material. The comparison sequences \( \{Y_i(k)\} (i = 1, 2, \ldots, \ldots, 8) \) were set based the volume fraction of particles in different grain sizes. Sequences \( \{Y_0(k)\} \) and \( \{Y_i(k)\} \) were then averaged. The results of average sequences \( \{X_i(k)\} \) and correlation coefficient sequences \( \{\xi_0(k)\} \) are shown in Tables 6 and 7, respectively, and Table 8 shows correlation degree between PG particle size and UCS.
Table 6. Results of average sequences.

| k | X₀ | X₁ | X₂ | X₃ | X₄ | X₅ | X₆ | X₇ | X₈ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.686 | 0.580 | 0.667 | 0.715 | 0.715 | 1.387 | 1.511 | 2.118 | 2.375 |
| 2 | 1.133 | 0.817 | 0.945 | 1.113 | 1.113 | 1.601 | 1.897 | 2.130 | 1.894 |
| 3 | 1.401 | 1.331 | 1.345 | 1.471 | 1.471 | 1.941 | 2.364 | 1.274 | 0.811 |
| 4 | 1.825 | 2.071 | 2.105 | 2.187 | 2.191 | 2.255 | 1.024 | 0.464 | |
| 5 | 2.431 | 3.421 | 4.031 | 4.058 | 4.058 | 1.548 | 0.670 | 0.105 | |

Table 7. Results of correlation coefficient sequences.

| k | ξ₁ | ξ₂ | ξ₃ | ξ₄ | ξ₅ | ξ₆ | ξ₇ | ξ₈ |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.931 | 0.999 | 0.999 | 0.916 | 0.634 | 0.595 | 0.456 | 0.414 |
| 2 | 0.799 | 0.875 | 0.992 | 0.981 | 0.725 | 0.613 | 0.556 | 0.614 |
| 3 | 0.958 | 0.970 | 0.986 | 0.912 | 0.694 | 0.556 | 0.914 | 0.674 |
| 4 | 0.839 | 0.819 | 0.747 | 0.729 | 0.773 | 0.742 | 0.601 | 0.468 |
| 5 | 0.575 | 0.454 | 0.437 | 0.435 | 0.874 | 0.603 | 0.430 | 0.363 |

Table 8. Correlation degree between PG particle size and unconfined compressive strength.

| Particle Size (µm) | <40 | 60 | 80 | 100 | 200 | 400 | 600 | >600 |
|--------------------|-----|----|----|-----|-----|-----|-----|-----|
| Correlation        | 0.821 | 0.824 | 0.832 | 0.835 | −0.740 | −0.622 | −0.590 | −0.507 |

To ensure precision of GRA results, two proportion types and different curing days of CPCM groups were tested. The correlation degree between the particle size and UCS of the CPCM mixed with a different ratio was as follows, as shown in Table 9, based on the same method that mentioned previously.

Table 9. Correlation degree between PG grades and unconfined compressive strength of cement–PG cementitious materials.

| Proportion | Curing Time | Particle Size (µm) | <40 | 60 | 80 | 100 | 200 | 400 | 600 | >600 |
|------------|-------------|--------------------|-----|----|----|-----|-----|-----|-----|-----|-----|
| Cement:PG = 1:1 | 3d | 0.816 | 0.819 | 0.821 | 0.833 | −0.731 | −0.616 | −0.572 | −0.504 |
| | 7d | 0.821 | 0.824 | 0.832 | 0.835 | −0.740 | −0.622 | −0.590 | −0.520 |
| | 28d | 0.834 | 0.847 | 0.867 | 0.871 | −0.789 | −0.641 | −0.613 | −0.521 |
| Cement:PG = 1:2 | 3d | 0.809 | 0.811 | 0.815 | 0.822 | −0.708 | −0.612 | −0.501 | −0.501 |
| | 7d | 0.819 | 0.820 | 0.822 | 0.829 | −0.721 | −0.618 | −0.551 | −0.506 |
| | 28d | 0.824 | 0.834 | 0.849 | 0.861 | −0.753 | −0.623 | −0.552 | −0.511 |

The correlation degree represents the relation between the comparison sequences and the reference sequence. The larger the absolute correlation degree value, the more significant is the relation between the comparison sequences and the reference sequence. Additionally, a positive relational polarity means that the relation is facilitation, whereas a negative polarity indicates an inhibiting effect. The key sieve pore size can thus be confirmed based on the GRA results, and then PG particle fineness can be obtained based on the key sieve pore, which is favorable for exploring the effect of PG particle fineness on cement–PG-stabilized material performance. The results of correlation degree between PG particle size and UCS of cement–PG cementitious materials show that different PG particle diameters seriously affect the UCS of cementitious materials.

It can be seen that the relational polarities between particles smaller than 200 µm and UCS were positive in each group, indicating that PG particles smaller than 200 µm can promote strength formation of cementitious materials. Additionally, the increase in the absolute value of the correlation degree illustrates that this promotion of strength was enhanced with increasing particle size. However,
relational polarities between particles larger than 200 µm and UCS were negative in each group, indicating that the formation of UCS was inhibited by particles larger than 200 µm and this inhibition effect was enhanced with decreasing particle diameter. This can be contributed to the change of specific surface area and impurities of PG caused by the changing fineness. The details can be found in Sections 3.2 and 3.3.

In conclusion, 200-µm PG particles have the most significant influence on the UCS of cementitious materials. Therefore, the key sieve pore size was determined as 200 µm based on GRA, and the fineness of PG refers to the summation of all sieve residues having screen aperture less than 200 µm.

Table 10 shows the fineness of PG at different grinding times based on the GRA results. It can be seen that there are large fineness differences under different grinding times, and that the fineness of PG fell sharply with an increase in the grinding time.

### Table 10. Fineness of PG particles at different grinding times.

| Grinding Time (min) | Particle Size (µm) | Fineness (%) |
|---------------------|--------------------|--------------|
|                     | <40                | 60           | 80 | 100 | 200 | 400 | 600 | >600 |
| 0                   | 2.52               | 4.90         | 9.55 | 26.80 | 19.01 | 18.45 | 10.24 | 8.53 | 56.23 |
| 5                   | 4.86               | 7.56         | 13.39 | 27.42 | 18.12 | 17.35 | 7.89  | 3.41 | 46.77 |
| 10                  | 6.28               | 10.89        | 16.46 | 27.34 | 15.89 | 15.46 | 5.28  | 2.40 | 39.03 |
| 15                  | 8.72               | 14.51        | 19.63 | 27.58 | 13.12 | 13.19 | 2.41  | 0.84 | 29.56 |
| 20                  | 10.75              | 17.83        | 22.72 | 28.91 | 10.16 | 7.43  | 1.71  | 0.49 | 19.79 |
| 25                  | 12.71              | 19.84        | 24.71 | 30.43 | 7.41  | 3.67  | 1.12  | 0.11 | 12.31 |

3.2. UCS

Figure 1 shows the 7-days unconfined compressive strength of cement–PG cementitious materials and cement–PG stabilized soil at different pH values, respectively. The group mixed with un-treatment PG was regard as control group, the pH value of it is about 3. All the six group specimens showed similar trends: When pH was less than 3, the UCS of the materials increased slowly; when the pH was increased from 3 to 5, the UCS in each group increased significantly with pH; and when the pH value was greater than 5, the increase rate of UCS decreased rapidly with increased pH and the UCS finally reached stabilization. Taking the M1 group cementitious material as an example, the specimen’s UCS increased from 4.38 to 4.56 MPa as the PG pH value increased from 2 to 3, with an increment of 0.18 MPa. When pH was increased from 3 to 5, the UCS increased from 4.56 to 6.68 MPa, and the increment increased sharply from 0.18 to 2.12 MPa. However, when the pH continued to increase to 8, the UCS slowly increased from 6.68 to 7.32 MPa, an increase of only 0.64 MPa, and ultimately reached a constant level. The average UCS of cement PG stabilized soil at pH value of 5 is as 1.3 times of control group. This indicates that pH value of PG can seriously affect the strength property of cement PG stabilized materials, when the pH value of PG reached 5, the best strength property of cement stabilized materials can be attained.

The above results are possibly attributed to the impurities in PG as different types and contents of impurities in PG can seriously affect cement–PG stabilized materials’ property. Acid soluble phosphorus, eutectic phosphorus, organic matter, and fluoride are the main impurities affecting PG properties [31,32]. Among these impurities, P₂O₅ has the most serious impact, the presence of P₂O₅ can significantly decreases PG’s activity. It is a soluble phosphorus impurity adsorbed on the surface of PG calcium sulfate dihydrate crystals, which coarsens the calcium sulfate dihydrate crystals and turns their original needle shape to rod-like or tabular shape. The P₂O₅ content in PG reduced with pH increased. When the pH value was less than 3, P₂O₅ content remained basically constant; thus, the UCS value increased slowly. When the PG pH value increased from 3 to 5, the P₂O₅ content fell sharply, leading to a great increase in the UCS. As the pH continued to increase, the content of P₂O₅ was neglectable and no longer reduce. Thus, it was difficult to impact PG properties significantly, which led to a constant UCS level of PG cement stabilized materials.
Figure 1. 7-day unconfined compressive strength (UCS) of CPCM and cement-PG stabilized soil at different PG pH values.

The UCS values with different PG particle fineness are graphically presented in Figure 2. The results show a continuous increase in the UCS with a reduction in PG fineness of each specimen when fineness decreased from 56.23% to 19.79%. However, with a further decrease in fineness, the rate of increasing UCS decreased sharply, and the UCS essentially reached its peak and kept stability as PG fineness decreased to 19.79%. Thus, UCS of cement stabilized soil can be considered as stable when fineness reached around 20%, with an average value of 1.5 times of the control group (mixed with ungrained PG).

Figure 2. 7-day UCS of cement–PG cementitious materials with different PG fineness.

The possible reasons for this can be contributed to that the smaller fineness of PG particles led to a larger specific surface area for PG particles. The reaction between calcium sulfate dihydrate crystals in PG and soil particles mainly occurs on the surface; therefore, the speed and extent of the reaction between calcium sulfate dihydrate crystals and soil particles and cement increased with decreased fineness, which caused an increase in the unconfined compressive strength of cement–PG-stabilized soil. But when the particle size of PG is too small, the reaction between water and cement are kinetically hindered, which go against to the formation of UCS, so the UCS kept stability when fineness decreased to 20%.
3.3. CBR

CBR value is a significant parameter to evaluate the strength ability of various road subgrade materials. Figure 3 illustrates the CBR value of cement–PG-stabilized soil as a function of the PG pH value. The CBR value of each specimen at different pH showed similar changing trend as UCS. Taking the M5 group as an example, as the pH changed from 2 to 3, the CBR value increased slowly with 4.1% from 280.2% to 284.3%. When the pH kept increasing from 3 to 5, the CBR value soared from 284.3% to 366.4% with an increase of 82.1%. However, when the pH value kept increasing and reached 8, the CBR value basically reached maximum values at 380%, showing increase of 13.1%. This could be related to the same explanation that was highlighted for unconfined compressive strength (Section 3.2), that the impurity content changed with pH value and the discrepancy of impurity content can differ greatly in mechanism property of stabilized soil.

![Figure 3. CBR value of cement–PG-stabilized soil as a function of the PG pH value.](image)

The CBR value of cement–PG-stabilized soil with different PG fineness are demonstrated in Figure 4. The CBR value of cement-PG stabilized soil increased with a reduction of PG fineness. The rate of increase of CBR value decreased sharply as PG fineness reached approximately 20%. Taking the M5 group as an example, when the PG fineness decreased from 56.23% to 19.79%, the CBR value increased 52.6% from 295.9% to 348.5%, with an average increase rate of 1.4. However, with a continuous decrease in fineness from 19.79% to 12.31%, the increase rate of CBR value is negligible with a figure of 0.17. It can be seen that the CBR of stabilized soil reached its peak at the fineness about 20%, averagely increased 1.4 folds compared to the control group.

This could be the same reason mentioned in Section 3.2 for UCS. Additionally, Peng [32,33] found that there are differences in the content of impurities in different particle size ranges. Purities like soluble phosphorus, organic matter, and F− mainly exist in the surface of PG particles, so the content of purities reduced with decreased PG fineness, which is beneficial to the strength-forming process of cement–PG-stabilized soil. When PG fineness continued to decrease below 20%, the content of impurities basically remained constant, causing lack of variance in CBR value. Considering construction cost, to gain a better CBR value of cement PG stabilized soil, the fineness of PG should be around 20%.
3.4. Establishment of Road Usage PG’s Classification Standard

Purities can seriously affect PG properties, but the content of it is difficultly detected in practical engineering, since it incurs high examination costs and complicated process; however, it can be seen that the mechanical properties have close relation of PG’s pH and fineness from Sections 3.1–3.3. The CBR and UCS of the cement–PG-stabilized materials increased with a reduction in PG fineness or growth of PG pH, and the pH value and fineness of PG is tested far more simply and conveniently in comparison to the purity test. Thus, PG pH and fineness can be therefore used to assess the properties of PG used in cement–PG-stabilized materials as indicators.

Adherent moisture content of an-grade phosphogypsum as building materials should not exceed 15% and its calcium sulphate dehydrate (CaSO$_4$·2H$_2$O) content should exceed 90% in accordance with GB/T 23456-2018 [33]. Meanwhile, the mechanical properties of the cement–PG-stabilized materials basically reached stability when the PG fineness decreased to 20% or the pH increased to 5. It is means that PG met its demarcation point of performance since PG’s pH reached to 5 or fineness decreased to 20%. Thus, classification standard of road usage PG was established based on the combination between mechanical analyses and above existing specification, as presented in Table 11. This proposition of classification standard of road-using PG has great significance on disposing and selecting PG used to stabilize subgrade soil.

| Grade | CaSO$_4$·2H$_2$O Content (%) | pH  | Fineness (%) | Adherent Moisture Content (%) |
|-------|-----------------------------|-----|--------------|-----------------------------|
| I     | ≥90                         | ≥5  | ≤20          | ≤15                         |
| II    | <90                         | <5  | >20          | >15                         |

According with the standards, PG can be defined as the I grade PG when the following four conditions are satisfied simultaneously: pH value of PG is larger than 5, fineness of PG is less than 20%, the CaSO$_4$·2H$_2$O content of PG is larger than 90% and adherent moisture content of PG is larger than 15%. The mechanical properties of cement-stabilized soil can be improved significantly when the I grade PG is used in the stabilization of subgrade soil.

4. Conclusions

An experimental study was carried out to study the effect of PG’s pH and fineness on performances of PG-cement-stabilized soil. Additionally, a road usage PG classification criterion was built based on unconfined compressive strength and California bearing ratio tests of PG-cement-stabilized materials.
The study resulted in the following conclusions. All the key information from the application conclusions can also be seen at the resume Table A1.

- A particle size of 200 µm can be used to determine PG fineness based on the key sieve pore size obtained from GRA. PG particles smaller than 200 µm promote the impact on the unconfined compressive strength of cement–PG cementitious materials, while those larger than 200 µm show inhibition. Additionally, the relevance between them is stronger when the particle size is closer to 200 µm.
- Both the CBR value and unconfined compressive strength of CPCM and cement-PG stabilized soil increased with PG pH values, and the increase rate tended to stabilize once the pH value reached 5.
- With a decrease in PG fineness, the results showed increased CBR value and UCS of CPCM and cement-PG stabilized soil. However, when PG fineness was less than 20%, the mechanical properties of cement–PG-stabilized material reached their peaks.
- A classification standard of road using PG was established based on indicators of CaSO₄·2H₂O content, pH, fineness, and adherent moisture content. The classification standard includes two grades (i.e., I and II), as shown in Table 10. Cement stabilized soil mixed with the I grade PG increased 1.3–1.5 fold of mechanical properties compared to that mixed with untreated PG.

Note that considering the complexity of the experiments, to simply the experiment process, this study used the same key sieve pore size for cement–PG-stabilized soil as that used for cementitious materials. Additionally, eight types of particle size sequences were considered in GRA, and thus, the division of sequences can be more detailed, with more particle size types being divided to gain a better analysis of the key sieve pore size. More details on the pH value and PG fineness can be obtained in the future, which will possibly enable them to be taken as PG property grade index for utilization of PG mixed with other materials in road engineering.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

All the key information from the application conclusions in the research can be seen at the resume Table A1.

|   | Key information from the application conclusions. |
|---|--------------------------------------------------|
| 1 | PG can be used in subgrade to stabilize soil with cement. |
| 2 | PH and fineness of PG have significant effects on the mechanical properties of cement-PG stabilized materials. |
| 3 | A particle size of 200 µm can be used to determine PG fineness. |
| 4 | The properties of subgrade soil can be improved significantly when the I grade PG is used in the stabilization of subgrade soil. |
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