Research Article

Optimization of Ionic Soil Stabilizer Dilution and Understanding the Mechanism in Red Clay Treatment

Xuesong Lu,1 Jin Luo,2 and Meinan Wan1

1School of Architectural Engineering, Huanggang Normal University, Huanggang 438000, China
2Faculty of Engineering, China University of Geosciences, Wuhan 430074, China

Correspondence should be addressed to Jin Luo; jinluo@cug.edu.cn

Received 17 December 2019; Revised 11 December 2020; Accepted 21 January 2021; Published 3 February 2021

Abstract

Due to the insufficient understanding of the mechanism for soil strengthening by using Ionic Soil Stabilizer (ISS), the application of ISS in soil treatment is limited. In this paper, red clay samples were treated by using ISS and the effects were examined by the Atterberg test and uniaxial pressure test. In order to understand the mechanism, ISS dilution-based seepage test and ξ-potential test have been carried out. The results show that the ISS-Water mixture of 1:200 was the most effective ratio to reduce the plasticity index. The measurements indicate the thickness of the pair-electricity layer of adjacent clay layers and the repulsion force among soil particles is reduced, which in turn enhances the attraction force of the clay layers. This process strengthens the connection among the soil particles and thus increases the strength of the soil as detected by the experimental tests.

1. Introduction

The red clay was widely distributed in southern China and it is often used as building materials or natural foundations of buildings. Since the red clay has swell-shrink characteristics and high plasticity index [1–3], it often induces many geo-hazards such as road cracking, uneven foundation settlement, slope instability, pit deformation, and destruction [4–6]. It was realized that the traditional soil solidifying materials such as cement, lime, and flyash had drawbacks of high costs and long construction periods, which could not meet the needs of the construction and social development [7, 8]. In order to increase the strength and reduce the deformation of the red clay, the Ionic Soil Stabilizer (ISS) was considered as an alternative. ISS is an anionic surfactant with a pitchy liquid at normal temperature, soluble in water, and with high electric conductivity. It mainly contains the active ingredient of sulfonated oil and has a unique duality in structure. Its high molecular structure is hydrophilic on one side and hydrophobic on the other side. The ISS mainly reduces the thickness of the Adsorbed Water of the clay particles through a series of physical-chemical reactions. Due to its advantages such as low cost, ecological environment friendliness, and fast in field construction, it has attracted much attention in recent years. It can be widely applied in engineering fields such as roads and building foundations [9, 10].

Many previous works had been done to investigate the characteristics and reinforcement mechanism of the effects of red clay treatment. There are mainly three achievements: (1) The research on improving the strength of the soil by ISS: for soil with the clay particle content of more than 25%, the soil becomes more compact and easy to be consolidated after ISS treatment, and hence to reduce porosity, increase density, better water stability, and improve the strength of the soil [11, 12]. Several studies examined the strength of red clay in Jishan of Guangdong province of China which was treated by ISS. Uniaxial strength tests were implemented and the findings showed that the soil was reinforced effectively [13, 14]. Meanwhile, some studies analyzed the change of microstructure of the soil samples to understand the enhancement of soil strength [15]. Two types of ISS including ZDYT-1 and ZDYT-2 were deployed. The strain-stress development was measured, and the results showed that the soil was effectively reinforced [16, 17]. With the use of ISS,
together with other materials, such as lime and cement, the performance of ISS solidified soil was much better than that of traditional lime soil, and the strength properties and structural stability of soil were obviously enhanced [18]. (2) The research on reducing the thickness of the absorbed water of soils: some studies indicated that ISS was helpful in the reduction of soil specific surface area, decreasing expansion rate and Zeta potential, and thinning the thickness of the absorbed water [19, 20]. (3) Investigation on the mechanism of ISS-reinforced warm frozen soil: through a series of tests on indoor mechanics, physics, and mechanics, ISS was used to treat the warm frozen soil and the mechanism on strengthening the warm frozen soil [21, 22]. Some studies have explored the reinforcement effect and application evaluation on the reinforcement soil and coal of the Liquid Ionic Stabilizer [23, 24] and elaborated on the mechanism of Liquid Ionic Stabilizer [25, 26]. By using ISS to treat landslide soil, the shear strength of landslide soil was tested and explored. Through laboratory experiments, the viscosity of landslide soil was obviously improved, and the mechanism of strengthening soil by ISS was explored [27, 28]. Some scholars also believed that the stability mechanism of ions might be achieved by exchanging cation and the increasing concentration of cation in soil pore water [29].

Most of the previous studies have been carried out on the reinforcement of soil using the ISS, but they rarely consider the optimization of the mixture ratio and the physical-chemical mechanisms. Thus, the mechanism of ISS-reinforced soil was insufficiently understood. This paper implements a series of physical mechanics and electrochemistry experiments to optimize the mixture ratio of ISS dilution and to understand the mechanism of clay reinforcement by seepage tests.

2. Materials and Study Methodology

2.1. Physical Property of the Samples. The samples were collected from Wuhan City of Hubei province, which is located in the middle of China. The soils show reticular characteristics, red and white color, with burying depth that varies from 1 m to 3 m. The soil samples were prepared to match the natural properties such as water content [30], plastic limit, and liquid limit of the red clay (see Table 1). Siphon specific gravity method is applied to determine the granularity distribution and the measurements are displayed in Table 2.

Tables 1 and 2 show that the red clay samples have a high liquid limit, high plastic limit, high content, and low density of viscous particles, and has a moderate-weak expansion.

2.2. Ionic Soil Stabilizer. ISS was first developed by Reynolds in American in 1959. It was named Reynolds Roadpacker on the market and widely applied worldwide later on. Since the 1960s, ISS was gradually introduced to Canada, Mexico, Australia, South Africa, and many other countries. The reinforcement technology of ISS provides a civil engineering construction method, and it has the advantages of low cost, easy to be constructed, local materials, and protection of the ecological environment; then it was widely used in the construction of roads, airports, building foundations, and water conservancy.

ISS is a surfactant-type soil stabilizer. It is pitchy with high electric conductivity at normal temperature. It can be soluble in water and dissociate positively charged cations and anions. ISS is a compound chemical formula containing the active ingredient sulfonated oil. Sulfonated oil is an anionic surfactant with a higher molecule and electric charge on adjacent bonds. It has a unique duality in structure and is made up of the “hydrophilic head,” which is an organic compound called sulfonic acid (RSO₃H, which is formed by directly connected a sulfonate group (-SO₃H)) and a carbon atom of a hydrocarbon group (R-H) and a “hydrophobic tail” consisting of carbon and hydrogen atoms.

ISS can be applied in soil treatment with varying particle sizes. Many practices have proved that the ISS can not only increase its compaction, density, carrying capacity, and cohesion but also improve the plasticity, the swell-shrink characteristics, and water sensitivity of the soil.

In this paper, in order to determine the optimal ratio of ISS for the red clay treatment, the ratios of ISS to water of 1 : 50, 1 : 100, 1 : 150, 1 : 200, 1 : 250, 1 : 300, 1 : 350, 1 : 400 were prepared.

3. Experimental Setup

This section is to examine the effects of ISS on the change of properties of red clay. Atterberg test was implemented to understand the physical property variation and the uniaxial compressive strength test was examined for shear changer enhancement. In order to further understand the mechanism, zeta potential and cation exchange in seepage were tested.

3.1. Atterberg Test. In order to determine the liquid limit and plastic limit test of red clay with different ISS ratios [30], the soil samples are tested before and after the treatment by ISS. The experiment can be divided into the following steps: First, scatter ISS dilution with different ratios evenly in the red clay. Secondly, beat red clay and ISS dilution with low speed until well combined. Thirdly, put the mixture in a plastic bag and maintain it 48 hours at pressurized canisters. Lastly, the liquid limit and plastic limit were measured.

3.2. Uniaxial Compressive Strength Test. A uniaxial compressive test was carried out to examine the strength of the soil samples [31]. The ISS dilution was added to the samples and maintained for 24 hours in a loose state. The ISS-treated samples were then adjusted to the optimized water content. Lastly, the samples were prepared and put the mixture in pressurized canisters for 24 hours. Before the strength test, the standard compaction test was carried out on the original and ISS-reinforced soil samples [32]. To ensure the uniformity of the samples, the static pressure method was used for sampling preparation. The specimens were cylinder-shaped with 50 mm diameter and 50 mm height. The specimens were wrapped in plastic sheeting and
immediately placed in a standard conservation box (with humidity of 95%, temperature of 20 ± 2°C, for 7 days, 14 days, 28 days, and 60 days).

3.3. Zeta Potential Test. The clay particles of original red clay and red clay treated with different ratios of the ISS solution are, respectively, extracted by water sedimentation analysis. Then, the clay particles were placed in the sample tank. The ξ potential test (device type: ZS90, UK) was carried out according to the procedure of instrument operation. In order to ensure the contrast of results, the water used must be pure water and the dispersing agent such as sodium hexametaphosphate must not be used in the process of extracting the clay into the dilution. The ξ potential should be tested immediately after clay particles are extracted because the faces may attract to each other to form a granule group when the clay particles move irregularly at sedimentation in the fully static condition for a long time. It is also possible to further form flocculation by gravitation between the single particle and the granule group.

3.4. Analysis of ISS Clay Treatment by Seepage Test. The reaction between ISS and soil is a complex physico-chemical process in a porous medium with multicomponent reactive solute transport. Since the surface of clay particles was negatively charged, cation on the particle surface was exchangeable. Therefore, the cation exchange and ion adsorption become the main reaction type affecting ion transport in the solution. In order to understand the reaction mechanism, the ion components of anion and cation in leaching solution is analyzed at different seepage periods. Specifically, the ion exchange between ISS dilution and red clay and the migration laws of cations such as K⁺, Na⁺, Ca²⁺, and Mg²⁺ in solution varied with time were examined. The hydrated film on the surface of the clay particles changes by the ISS treatment can then be revealed.

During the experiment, the leaching solution at different stages by the day was collected. The electrical conductivity was measured to investigate the changes in the chemical reaction process. Finally, the anion and cation of five representative samples are determined. The G-01H denotes the water sample in the early stage of the pure water seepage. Before the ISS dilution seepages through the red clay sample, the soil sample had been filtered by pure water for 6 days. The conductivity of the leaching solution was measured less than 15 uS/cm, which is similar to pure water. It indicates that the soluble salt in the red clay is substantially dissolved. GI-02H is a leaching solution on the second day after the infiltration of ISS dilution. The electrical conductivity increased rapidly compared with GI-01H. Although the total amount of ion is not high, it proves that there was an ion exchange between ISS and the soil. This sample of leaching solution can reflect the state of the initial reaction between ISS and the soil. This sample of GI-04H is chosen because its conductivity increased rapidly. Moreover, the conductivity has remained stable for a while. The samples No. GI-15H and GI-17H were also selected and the degree of reaction can be observed by test the conductivity of these two samples. The instructions for the sample of leaching solution are shown in Table 3.

3.5. Energy Spectroscopy Test. The chemical composition of red clay before and after the treatment by ISS was analyzed by environmental scanning electron microscope equipped with energy dispersive spectrometer (EDS) (type: Quanta 200FEG, FEI company, Netherlands).

4. Results and Discussion

To understand the effects of ISS on red clay treatment, Sections 4.1–4.3 are presented to show the physic-mechanical properties changes. The statement of the optimized ration of the ISS dilution was made by considering the uniaxial strength of the specimens. Furthermore, the mechanism of the ISS treatment on red clay was investigated in terms of zeta potential, ionic exchange, and micromorphological variation, as shown in section 4.4–4.7.

4.1. Plasticity Index. The plasticity index is one of the most important indexes to determine the physical property of clay soil. The plasticity index reflects the particle size, the content of clay or hydrophilic mineral, and the hydrophilic properties of the soil. The greater the plasticity index, the higher content of clay and hydrophilic mineral is expected. The thicker the hydrated film is combined, the larger the ranges of water content in the plastic state, indicating the lower strength of the soil and vice versa [33].

Table 4 shows that the liquid limit, plastic limit, and plasticity index are all reduced when the red clay was treated by ISS. The plastic limit and plasticity index of red clay are dropped to the lowest level under the ISS-water ratio of 1:200. The plasticity index of ISS-treated red clay can be

### Table 1: Physical property of red clay samples.

| Moisture content (%) | Density (g·cm⁻³) | Specific gravity | Liquid limit W_L (%) | Plastic limit W_P (%) | Plastic index I_p (%) | Free swelling ratio (%) |
|----------------------|------------------|------------------|----------------------|----------------------|----------------------|------------------------|
| 24.81                | 1.92             | 2.76             | 57.86                | 24.27                | 33.59                | 60                     |

### Table 2: Particle size distribution and its ratio of red clay samples.

| Particle size (mm) | Content (%)<5 | <2 | <1 | <0.5 | <0.25 | <0.075 | <0.05 | <0.01 | <0.005 | <0.002 |
|--------------------|---------------|----|----|------|-------|--------|-------|-------|--------|--------|
|                    | 100           | 99.78 | 99.69 | 99.46 | 99.32 | 98.72 | 89.08 | 58.94 | 47.25 | 42.92  |

### Table 3: Particle size distribution and its ratio of red clay samples.
controlled at 28.84%, which is 14.14% lower than the original red clay. Below this point, the plastic index keeps decreasing with increasing the ratio. In contrast, the plasticity index increases with enlarging a mixture ratio when the concentration ratio of ISS is higher than 1:200.

4.2. Strength of Red Clay Treated Using ISS. Uniaxial strength tests were implemented and the results are displayed in Table 5. Correspondingly, the development of unconfined compressive strength with varying curing period under the different ISS ratios is presented in Figure 1.

In practice, the unconfined compressive strength at 7 days is often used to determine the optimal ratio of ISS. It can be seen from Table 5 that the unconfined compressive strength is significantly improved by adding ISS to red clay. When the ratio of ISS to water is 1:200 (volume ratio), red clay has the highest unconfined compressive strength of 349 kPa at 7 days, which is 36.86% higher than the unconfined compressive strength of the raw sample. Similarly, the plasticity index of red clay at different ISS ratios shows the same trend with the compressible strength observed. The higher the plasticity index, the thicker the hydrated film and the larger the distance between the particles, indicating a weaker bonding force and vice versa [33].

It can be seen from Figure 1 that the strength of ISS solidified soil increases with the curing period. The strength increased rapidly during 0–28 days and slowed down after this period. This could be attributed to two reasons: one is the surface contact of clay particles after adding ISS solution. The other is the hydraulic permeability of red clay is extremely low. It takes time for ISS to diffuse and seep into the interior of the soil and fully react with most of the soil particles.

4.3. Optimization of ISS Dilution. The repulsive force between the soil particles was reduced and the attraction was increased. Thus the soil becomes denser and the strength of the soil is increased. Therefore, the optimal ratio of ISS-reinforced red clay could be determined by combining the minimum plasticity index and unconfined compressive strength [15, 34, 35].

Tables 4 and 5 show that the plasticity index of red clay is minimized, and the unconfined compressive strength reaches the maximum under the ratio of ISS to water is 1:200 (volume ratio). Therefore, one of the above two indicators can be used to determine the optimal proportion of ISS-reinforced soil in practical application.

The ISS dissociates the positively charged cation \([X]^{n+}\) and the negatively charged anion \([Y]^{n–}\) in water. By adding ISS into the red clay, it can replace the exchangeable cation adsorbed on the surface of the clay. The pair-electricity layer on the surface of clay particles is changed and the thickness of hydrated film becomes thinner. Since the ISS has a slightly higher viscosity than water, it seeps slower than that of pure water in the soil matrix. In addition, the permeability coefficient of red clay remains very small, and when the ISS concentration is high, it is extremely slow to exchange cations in the soil. When the ISS concentration is too low, the amount of cations \([X]^{n+}\) dissociated by ISS in water is insufficient. The exchange reaction with the exchangeable cations in the soil is not thorough enough and the effect of strengthening is low. Therefore, it is necessary to control the amount and the ratio of ISS in practical application.

4.4. Zeta Potential. The \(\xi\) potential of red clay reinforced by ISS is displayed in Table 6. The \(\xi\) potential analyzer (Type: Zetasize Nano ZS90, Malvern company, UK) was applied to measure the particles sizing range between 3 nm and 3000 nm in this test.
The potential values of red clay reinforced by ISS are negative and this indicates that the surface of the clay particles of the raw red clay samples and ISS-reinforced red clay samples are all negatively charged. In the vicinity of the broken bond of red clay particles, there may be a small amount of positive charge. However, the amount is much smaller than the negative charge on the surface of clay mineral particles. Therefore, the net charge of clay minerals is still negative, as the net charge is an algebraic sum of positive and negative charges. Since the negative charge of clay minerals is generally greater than the positive charge, clay minerals generally exhibit a negative charge. The potential of the red clay can still be detected after ISS treatment, indicating that ISS can only reduce the thickness of the electric double layer, but it cannot eliminate the pair-electricity layer structure.

As shown in Table 6, the potential values (absolute value) of red clay are obviously reduced by deploying ISS. At the optimal ratio of ISS to water (volume ratio), which is 1:200, the potential value of red clay is reduced from −31.02 mV to a minimum −17.62 mV, declining by 43.2%. In addition, the potential value of red clay reinforced by ISS is not proportional to the concentration of ISS. With the ISS concentration increase to a certain value, the potential value increases again. Comparing the potential values with ISS concentration, a similar trend was presented. In ISS-treated red clay, the greater the soil plasticity index, the smaller the potential value, and vice versa. The potential can reflect the thickness change of absorbed water. As the potential increases, the absorbed water becomes thicker, the hydrophilicity of soil is stronger, and the corresponding plasticity index is higher. The thickness of the absorbed water has a great influence on the physical and mechanical properties of clayey soil. Reducing the thickness of absorbed water on clay particles, the repulsive force was reduced as well and the attraction force between the soil particles was increased. Consequently, the soil particles become closer and therefore, the strength of the soil was enhanced.
4.5. Ionic Composition of Percolation. The dilution of leached solution from seepage tests was collected and tested by ion emission spectrometer (ICP-AES) for main cation composition and by ion chromatograph (DX-120) for anion composition. The variations of cation concentration are listed in Table 7, and the changes of anion concentration are shown in Table 8.

G-01H is the water sample in the early stage of the pure water seepage stage. It should be said that the soil contains soluble salts and it dissolves, as shown in Tables 7 and 8. The cations of soluble salts mainly include K+, Na+, Ca2+, and Mg2+. The concentrations of Na+ and Ca2+ are higher than those of K+ and Mg2+. Anions mainly include Cl−, NO3−, SO42− and a small amount of NO2− and F−.

In this paper, the variation of cation concentration such as K+, Na+, Ca2+, and Mg2+ during the ISS reinforcement process was considered, as shown in Table 9.

The analysis of various anion concentrations in sample GI-17H shows that the concentration of anion Cl−, NO3− and SO42− in the seepage leach tends to the same concentration in the primary period, as shown in Figure 2. ISS can dissociate positively charged cations and negatively charged anions in the water. If the anion concentrations and the corresponding cation concentrations in percolation leaching liquid are basically the same as those in ISS primary solution, it suggests that the cations dissociated from ISS in the water do not carry out cation exchange with cations adsorbed on the surface of clay particles. On the contrary, if the corresponding cationic concentration differs significantly from that of the ISS primary solution, a cation exchange reaction occurs.

After the pure water seepage, all solution samples at the seepage stage of ISS dilution were collected from sample G-01H to sample GI-17H. As it can be seen from Figure 3, when the seepage of ISS dilution goes in red clay, the concentration variation of a single cation in the leach solution is as follows: K+ has little change due to its very small concentration; the ion concentration of Na+, Ca2+, and Mg2+ increases significantly; and the final Ca2+ and Mg2+ ion concentration is much higher than that of the ISS original solution, while the Na+ ion concentration decreases compared with that of the ISS original solution (sample GI-17H). Consequently, the concentration of cation Na+, Ca2+, and Mg2+ in the leach differ significantly from the original ISS solution, while the concentration of anion is similar to that of ISS original solution. It implies that the cation in dilution of ISS performs ion exchange with the cations adsorbed on the surface of red clay particles. The concentration of Na+ in the seepage leach in sample GI-17H decreased, indicating that some Na+ was intercepted by clay particles and absorbed, while the concentration increase of Ca2+ and Mg2+ is owing to the desorption of Ca2+ and Mg2+ from clay particles after the adsorption of Na+ ions.

In order to further analyze the adsorption and exchange capacity of several main cations, we convert them into milligram equivalent for comparison. Milligram equivalent (mEq) is the amount of chemical activity or resultant force of a substance equivalent to 1mg of hydrogen, i.e., 1mg H, 23mg Na, 39mg K, 20mg Ca, 12mg, and 35mg Cl are all 1mEq. The data obtained by converting K+, Na+, Ca2+, Mg2+ and Na+/Ca2+, Na+/Mg2+ are shown in Table 10. Since K+ concentration and its variation are very small, K+ is not considered here. To investigate the cation exchange between ISS dilution and red clay, the variation trend of the Na+/Ca2+, and Na+/Mg2+ in exudates with time is shown in Figure 4.

The variation trend of Na+/Ca2+, and Na+/Mg2+ ratio are first up and then down as the penetration curing, as shown in Figure 4. The reason is that a certain amount of soluble salt in the red clay dissolved corresponding to a rising trend in the early stage. Then along with the cation exchange reaction, a portion of the Na+ was intercepted and adsorbed by clay, while Ca2+ and Mg2+ was desorbed from the clay particles corresponding to the declining trend. Accordingly, Na+ ions in ISS aqueous have cation exchange with Ca2+ and Mg2+ ions adsorbed on the surface of clay particles.

4.6. Micromorphology and Chemical Composition Analysis. The micromorphology of red clay before and after treatment is shown in Figure 5 (a1, a2), and the associated energy spectrum of red crossing points (A and B) is illustrated in Figure 5 (a2, b2). The chemical composition of the microzone at point A and point B is illustrated in Table 11.

Table 11 shows that the C element appears in red clay after being reinforced by ISS, while other elements decrease relatively. The appearance of element C is ascribed to the organic components in ISS. Due to the chemical chain interaction between SO32− ions in the “hydrophilic head” of ISS and cationic adsorbed on the surface of clay particles, ISS combines with red clay particles, and its “hydrophobic tail” forms an oily layer around clay particles, making soil particles hydrophobic. Since the “hydrophobic tail” part of ISS contains a C element, a C element can be found on the surface of soil particles in the solidified sample, while there is no such element in the original sample of red clay. Thus, the existence of “hydrophobic tail” in ISS is further identified by the energy spectrum test of soil samples, which is one of the important reasons for improving the engineering characteristics of the soil.

4.7. Reinforcement Mechanism of ISS on Red Clay. The decrease of ξ potential indicates the attenuation of absorbed water film around the clay particles. Analyzing the cation exchange reaction process between ISS aqueous and red clay, low-valence state Na+ ions was the major agent in the reaction. The Na+ ion exchange corresponds to a decrease in the thickness of the diffuse double layer.

The exchange capacity of cation mainly depends on the ionic valence, ion radius, and ionic concentration, and it influences the thickness of diffusion double layer. The exchange capacity of a high valence state cation is stronger than that of a low-valence state cation. In monovalent ions, the exchange capacity of a small radius is weaker than that of a large radius. But when the cation concentration is large enough, the low-valence state cation can also exchange for high valence state cation. In the system, whether the ion with the opposite sign (an ion with the same sign as the particle...
surface charge) or the same sign has an effect on the electric potential, especially for the ion with the opposite sign [36].

According to the ion composition analysis of ISS aqueous-red clay, some amount of Na⁺ in ISS aqueous was intercepted and adsorbed in red clay, while Ca²⁺ and Mg²⁺ ions were desorbed, which was due to ion exchange between high concentration Na⁺ in ISS solution and Ca²⁺ and Mg²⁺ ions on the clay particle surface. When other conditions remain unchanged, the diffusion double layer of ions with low valence is thicker than that of ions with high valence, and vice versa. Here, the high-valence Ca²⁺ and Mg²⁺ ions were replaced with low-valence Na⁺ ions, which should predict the thickening of clay particle diffusion double layer added with ISS. However, it is the opposite of ξ experiments results that the thickness of diffusion double layer around clay particle reduced, and the absorbed water film became thinner.

The ISS is a compound organic chemical that contains the active ingredientsulfonatedoil. Sulfonated oil consists of a "hydrophilic head" (R-SO₃H) of an organic compound called sulfonic acid and a "hydrophobic tail" consisting of C and H elements. "Hydrophilic head" is soluble in water but insoluble in most nonpolar organic solvents. "Hydrophobic tail" is completely insoluble in water but miscible in

---

**Table 7: Analysis of cation concentration of exudate.**

| Cationic species | G-01H (mg/L) | GI-02H (mg/L) | GI-04H (mg/L) | GI-15H (mg/L) | GI-17H (mg/L) | ISS dilution (mg/L) |
|------------------|--------------|--------------|--------------|--------------|--------------|---------------------|
| Al³⁺             | 0.013        | 0.018        | 0.019        | 0.018        | 0.018        | 0.007               |
| As³⁻             | 0.072        | 0.090        | 0.127        | 0.126        | 0.145        | 0.127               |
| Ba²⁺             | 0.018        | 0.048        | 0.118        | 0.262        | 0.308        | 0.100               |
| Be²³⁺            | 0.000        | 0.000        | 0.000        | —            | —            | —                   |
| Ca¹⁺             | 7.937        | 14.008       | 18.573       | 29.377       | 34.561       | 8.998               |
| Cd²²⁺            | —            | —            | 0.000        | 0.000        | 0.000        | —                   |
| Co²⁺             | 0.001        | 0.002        | 0.003        | 0.006        | 0.007        | 0.004               |
| Cr²⁻             | —            | —            | —            | 0.001        | 0.002        | 0.003               |
| Cu²⁺             | 0.019        | 0.009        | 0.011        | 0.038        | 0.042        | 0.286               |
| Fe²⁻             | —            | —            | 0.003        | 0.077        | 0.084        | 0.288               |
| K⁺               | 1.335        | 2.525        | 1.308        | 1.426        | 1.598        | 0.795               |
| Li⁻              | 0.002        | 0.037        | 0.065        | 0.203        | 0.227        | 0.075               |
| Mg²⁺             | 1.951        | 3.799        | 5.422        | 7.656        | 8.723        | 0.906               |
| Mn²⁵⁺            | 0.002        | 0.037        | 0.065        | 0.203        | 0.227        | 0.075               |
| Na⁵⁻             | 14.134       | 45.008       | 96.360       | 135.34       | 150.911      | 216.228             |
| Ni²¹⁺            | 0.005        | 0.002        | 0.002        | 0.005        | 0.006        | 0.013               |
| P₂⁻              | 0.008        | 0.015        | 0.015        | 0.023        | 0.028        | 0.063               |
| Pb²⁺             | 0.021        | 0.017        | 0.026        | 0.022        | 0.019        | 0.084               |
| S₁⁻              | 7.859        | 71.860       | 146.000      | 205.835      | 240.900      | 277.000             |
| Se²⁻             | 0.004        | 0.006        | 0.006        | 0.005        | 0.004        | 0.009               |
| Si²⁻             | 4.167        | 5.754        | 5.905        | 6.037        | 6.122        | 0.821               |
| Sr²⁺             | 0.056        | 0.106        | 0.143        | 0.158        | 0.250        | 0.035               |
| V₃⁻              | 0.065        | 0.074        | 0.079        | 0.086        | 0.099        | 0.049               |
| Zn²⁺             | 0.034        | 0.065        | 0.091        | 0.125        | 0.147        | 0.128               |

**Table 8: Concentration of main anions from the exudate in different periods.**

| Anion species | ISS dilution (mg/L) | G-01H (mg/L) | GI-02H (mg/L) | GI-04H (mg/L) | GI-17H (mg/L) |
|---------------|---------------------|--------------|--------------|--------------|--------------|
| Cl⁻           | 2.728               | 19.315       | 5.662        | 4.378        | 2.815        |
| NO₃⁻          | 0.204               | 8.546        | 0.214        | 0.21         | 0.209        |
| NO₂⁻          | —                   | 0.826        | 0.208        | —            | —            |
| SO₄²⁻         | 61.933              | 26.414       | 15.508       | 23.227       | 61.872       |
| F⁻            | —                   | 0.542        | 0.230        | 0.261        | 0.3312       |

**Table 9: Concentration of main cations from the exudate in different periods.**

| Cation species | ISS dilution (mg/L) | G-01H (mg/L) | GI-02H (mg/L) | GI-04H (mg/L) | GI-15H (mg/L) | GI-17H (mg/L) |
|----------------|---------------------|--------------|--------------|--------------|--------------|--------------|
| K⁺            | 0.795               | 1.335        | 2.525        | 1.308        | 1.426        | 1.598        |
| Na⁺           | 216.228             | 14.134       | 45.008       | 96.360       | 135.34       | 150.911      |
| Ca²⁺          | 8.998               | 7.937        | 14.008       | 18.573       | 29.377       | 34.561       |
| Mg²⁺          | 0.906               | 1.951        | 3.799        | 5.422        | 7.656        | 8.723        |
nonpolar solvents such as oil. Due to the duality of “hydrophilic head” and “hydrophobic tail” in ISS, when it is incorporated into the clay-water system, it shows unique characteristics: (1) When sulfonated oil is dispersed in water, this part of “hydrophilic head” can dissociate $\text{SO}_3^{2-}$ ion, and it can form a direct chemical chain with metal cation on the surface of red clay particles. (2) When an oxygen atom of $\text{SO}_3^{2-}$ in the ISS combines with a metal cation on the red clay particles, ISS occupies a cationic vacancy on the surface of the clay crystals. (3) “Hydrophilic head” dissolves in the absorbed water around the surface of clay minerals and adsorbs on the surface of clay minerals. The interaction process between ISS and clay particles is shown in Figure 6.

The interaction between ISS and red clay can result in the following consequences: (1) The cation which has great activity is bounded in the original place, which caused the “sealing effect” of ISS. It prevents ions from dissolving freely in the water. (2) ISS molecule combines with red clay particles, and its “hydrophobic tail” forms an oily layer (hydrophobic layer) around the surface of clay particles.

Table 10: Milligram equivalent of the main cations from the exudate in different periods.

| Ion species | ISS dilution (mEq) | G-01H (mEq) | GI-02H (mEq) | GI-04H (mEq) | GI-15H (mEq) | GI-17H (mEq) |
|-------------|--------------------|-------------|-------------|-------------|-------------|-------------|
| Seepage time (d) | 0 | 1 | 8 | 10 | 21 | 23 |
| $K^+$ | 0.02 | 0.034 | 0.065 | 0.034 | 0.032 | 0.041 |
| $Na^+$ | 9.401 | 0.615 | 1.957 | 4.190 | 5.884 | 6.561 |
| $Ca^{2+}$ | 0.450 | 0.397 | 0.700 | 0.929 | 1.469 | 1.728 |
| $Mg^{2+}$ | 0.076 | 0.163 | 0.317 | 0.452 | 0.638 | 0.727 |
| $Na^+/Ca^{2+}$ | 20.896 | 1.549 | 2.794 | 4.511 | 4.006 | 3.797 |
| $Na^+/Mg^{2+}$ | 124.519 | 3.780 | 6.181 | 9.272 | 9.223 | 9.026 |
Figure 4: Variation of Na\(^+\)/Ca\(^{2+}\) and Na\(^+\)/Mg\(^{2+}\) (milligram equivalent ratio) in the exudate during different periods.

Figure 5: Micromorphology and energy spectrum of the original red clay (a) and red clay reinforced with ISS (b).

Table 11: Elemental analysis of red clay before and after reinforcement with ISS.

| Sample point          | Element (Wt%) |
|----------------------|---------------|
|                       | C  | O   | Al  | Si  | K   | Fe  |
| A in original sample  | 0  | 35.45 | 15.75 | 34.97 | 2.44 | 11.39 |
| B in solidified sample| 22.12 | 30.94 | 11.03 | 27.69 | 1.70 | 6.52 |
Thus, the water in the red clay can be expelled by the “hydrophobic tail” without much mechanical pressure. In consequence, ISS can effectively reduce the thickness of the binding water of clay particles by the following four aspects:

(1) The “hydrophilic head” in ISS forms a chemical chain with the metal cation on the surface of clay particles. ISS molecules occupy part of the positions of hydrophilic cations adsorbed on the surface of red clay particles, and they adsorb on the surface of clay minerals.

(2) The “hydrophobic tail” in the ISS forms a hydrophobic layer around the surface of clay particles and inhibits water from entering the system.

(3) In a clay-water system, when there is a difference in cationic concentration between the clay mineral crystal layer and the solution, a “membrane effect” happens: the one with higher ion concentration absorbs water while the one with lower ion concentration loses water. ISS is a solution with a high ion concentration. When it comes into contact with the crystalline layer of clay minerals, it causes the clay minerals to remove water between the layers, thus reducing the interplanar spacing of clay minerals.

(4) The organic chains in the ISS solution form H bonds with oxygen at the bottom of the crystal layer. The H bond has a stronger attraction to negatively charged clay mineral crystal layers, making the crystal spacing more stable and less susceptible to changes in pore fluid properties.

In summary, the combination of physical interaction, physicochemical effect between ISS and red clay reduced the thickness of absorbed water on the surface of clay particles. This is conducive to the proximity and aggregation of clay particles. Thus, the soil strength was increased so as to solidify the red clay.

5. Conclusions

This paper aims to optimize the mixture ratios of ISS dilution and to reveal the mechanism of clay reinforcement by using the ISS dilution. The major findings of this paper include

(1) The physical properties such as liquid limit, plastic limit, and plastic index of red clay decreased by adding ISS mixtures into samples. The greatest reduction of plasticity index of the red clay of 14.14% was observed when the mixture ratio of ISS with water is 1:200.

(2) The strength of solidified soil increased with the testing duration for all the ISS dilutions. It rose rapidly in the period of 0 to 28 days and the trend to be lower increasing after 28 days.

(3) The $\xi$ potential value of red clay was reduced but still existed by ISS treatment, indicating that ISS can reduce the thickness of the electric double layer, but it can not eliminate the pair-electricity layer structure.

(4) The $\xi$ potential value of the red clay sample decreases from $-31.02 \text{ mV}$ to $-17.62 \text{ mV}$ by 43.2% under the optimized ISS dilution. In addition, the trend of plasticity index change was consistent with the $\xi$ potential value of red clay with different ratios of ISS dilutions.
(5) The change of ion concentration in the process of ISS dilution seepage through the soil sample was determined with time. The measurements show that four cations, including K⁺, Na⁺, Ca²⁺, and Mg²⁺, and the anions Cl⁻, NO₃⁻, and SO₄²⁻ were detected in the solutions. The variation of Na⁺/Ca²⁺ and Na⁺/Mg²⁺ ratio indicates that the Na⁺ ions in ISS dilution have cation exchanged with Ca²⁺ and Mg²⁺ ions adsorbed on the surface of clay particles.

(6) By considering the physicochemical interaction between ISS and red clay, the thickness of the absorbed water on the surface of red clay particles was reduced, thus, in turn, enhancing the strength of red clay.

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

Conflicts of Interest
The authors declare that they have no conflicts of interest.

Acknowledgments
The authors wish to acknowledge the financial support from the National Natural Science Foundation of China (Grant nos. 40972185 and 40672188).

References
[1] X. Chen, J. Zhang, Y. Xiao, and J. Li, “Effect of roughness on shear behavior of red clay - concrete interface in large-scale direct shear tests,” Canadian Geotechnical Journal, vol. 52, no. 8, pp. 1122–1135, 2015.
[2] J. Yuan, Y. He, and J. Liu, “Construction of weak expansive red clay on dongxin expressway in hunan province, China,” Journal of Performance of Constructed Facilities, vol. 30, no. 1, Article ID C4015001, 2016.
[3] H. Yuan, W. Li, Y. Wang, H. Lin, and Y. Liu, “Resilient modulus-physical parameters relationship of improved red clay by dynamic tri-axial test,” Applied Sciences, vol. 9, no. 6, p. 1155, 2019.
[4] Y. Q. Tang, K. Sun, X. H. Zhang, J. Zhou, Q. Yang, and Q. Liu, “Microstructure changes of red clay during its loss and leakage in the karst rocky desertification area,” Environmental Earth Sciences, vol. 75, no. 6, p. 537, 2016.
[5] Z. Zhang, T. Wang, S. Wu, H. Tang, and C. Liang, “Dynamics characteristic of red clay in a deep-seated landslide, Northwest China: an experiment study,” Engineering Geology, vol. 239, pp. 254–268, 2018.
[6] Y. Chen, B. Li, Y. Xu, Y. Zhao, and J. Xu, “Field study on the soil water characteristics of shallow layers on red clay slopes and its application in stability analysis,” Arabian Journal for Science and Engineering, vol. 44, no. 5, pp. 5107–5116, 2019.
[7] J. Li, K. Hao, and P. Feng, “Research on suction equilibrium time of unsaturated reticulate red clay,” KSCE Journal of Civil Engineering, vol. 22, no. 2, pp. 565–571, 2018.
[8] S. Yang, S. Wu, J. Lee, H. Lee, and S. Kim, “Biochar-red clay composites for energy efficiency as eco-friendly building materials: thermal and mechanical performance,” Journal of Hazardous Materials, vol. 373, pp. 844–855, 2019.
[9] Y. S. Cheng and J. J. Dong, Ionic Soil Stabilizer Book Series One: ISS Construction Guide, Wuhan University of Technology Press, Wuhan, China, 1999, in Chinese.
[10] Z. G. Wu, Z. C. Zhang, K. Q. Tong, and D. Xu, Applied by Ionic Soil Stabilizer in Flood Control Dam Works, Wuhan University of Technology Press, Wuhan, China, 2000, in Chinese.
[11] X. Y. Shen, S. J. Deng, and H. Cao, “Research on the application of ISS material in flood control road,” Yangtze River, vol. 34, no. 12, pp. 16–18, 2003, in Chinese.
[12] L. J. Zhang, Y. M. Wang, Y. K. Chen, H. Chen, and S. H. Tan, “Compactibility of soil stabilizer strengthening soil,” Journal of South China University of Technology (Natural Science Edition), vol. 32, no. 3, pp. 83–87, 2004, in Chinese.
[13] Y. M. Wang, L. J. Zhang, W. G. Su, and Y. Y. Hua, “Experimental study on ISS stabilized soil,” Highway, vol. 7, pp. 39–43, 2001, in Chinese with English abstract.
[14] L. J. Zhang, Y. M. Wang, W. G. Su, and P. Su, “Experimental research on the CBR values of the reinforced earth,” Journal of South China University of Technology (Natural Science Edition), vol. 30, no. 7, pp. 78–82, 2002, in Chinese.
[15] Y. M. Wang, J. Jia, L. J. Zhang, and Y. K. Chen, “Microstructure and strength feature of ISS stabilized soil,” Journal of South China University of Technology (Natural Science Edition), vol. 30, no. 9, pp. 96–99, 2002, in Chinese.
[16] Y. N. Dong, R. Q. Xu, and X. N. Gong, “The experimental research of the clay stabilized with solidified agent ZDYT-1,” Chinese Journal of Geotechnical Engineering, vol. 23, no. 4, pp. 472–475, 2001, in Chinese.
[17] Y. N. Dong, Q. E. Zhang, R. Q. Xu, and X. N. Gong, “Experimental study on strengthened soft clay with stabilizer ZDYT-2,” China Civil Engineering Journal, vol. 35, no. 3, pp. 82–86, 2002, in Chinese.
[18] B. Peng, W. Y. Li, and L. L. Dai, “Research on liquid stabilizer reinforced soil,” Journal of Xi’an Highway University, vol. 21, no. 1, pp. 15–18, 2001, in Chinese.
[19] Q. B. Liu, W. Xiang, W. F. Zhang, and D. S. Cui, “Experimental study of ionic soil stabilizer-improves expansive soil,” Rock and Soil Mechanics, vol. 30, no. 8, pp. 2286–2290, 2009, in Chinese.
[20] D. S. Cui, Research on the Reaction Mechanism of Adsorbed Water in Red Clay of Wuhan with Ionic Soil Stabilizer, China University of Geosciences, Wuhan, China, 2009, in Chinese.
[21] H. F. Zhang, H. Feng, J. G. Guo, F. Y. Wang, P. X. Wu, and D. Q. Wang, “Study on passivation of clay minerals and its mechanism,” Geological Journal of China Universities, vol. 6, no. 2, pp. 287–291, 2000, in Chinese.
[22] Z. L. Zhang, J. M. Zhang, and H. Zhang, “Effects and mechanisms of ionic soil stabilizers on warm frozen soil,” Arabian Journal for Science & Engineering, vol. 43, no. 2, pp. 5657–5666, 2008.
[23] W. Han, G. Zhou, Q. Zhang, H. Pan, and D. Liu, “Experimental study on modification of physicochemical characteristics of acidified coal by surfactants and ionic liquids,” Fuel, vol. 266, Article ID 116966, 2020.
[24] W. Han, G. Zhou, D. Gao et al., “Experimental analysis of the pore structure and fractal characteristics of different metamorphic coal based on mercury intrusion-nitrogen adsorption porosimetry,” Powder Technology, vol. 362, pp. 386–398, 2020.
[25] T. M. Petry and B. Das, “Evaluation of chemical modifiers and stabilizers for chemically active soils-clays,” Transportation
[26] L. E. Katz, A. F. Rauch, H. M. Liljestrand, J. S. Harmon, K. S. Shaw, and H. Albers, “Mechanisms of soil stabilization with liquid ionic stabilizer,” Transportation Research Record: Journal of the Transportation Research Board, vol. 1757, no. 1, pp. 43–49, 2001.

[27] W. Xiang, D. S. Cui, and L. Li, “Experimental study on sliding soil of ionic soil stabilizer-reinforces,” Earth Science, vol. 32, no. 5, pp. 397–402, 2007, in Chinese.

[28] H. Q. Xu, Research on Sliding Soil Reinforced by Ionic Soil Stabilize, China University of Geosciences, Wuhan, China, 2008, in Chinese.

[29] H. Zhao, L. Ge, T. M. Petry, and Y.-Z. Sun, “Effects of chemical stabilizers on an expansive clay,” KSCE Journal of Civil Engineering, vol. 18, no. 4, pp. 1009–1017, 2014.

[30] Nanjing Hydraulic Research Institute, SL237-1999 Specification of Soil Test, China Water Conservancy Hydropower Press, Beijing, China, 1999, in Chinese.

[31] Ministry of Transport of the People’s Republic of China, (JTGE51-2009) Test Methods of Materials Stabilized with Inorganic Binders for Highway Engineering, China People Transport Press, Beijing, China, 2009, in Chinese.

[32] Ministry of Transport of the People’s Republic of China, (JTGE40-2007) Test Methods of Soils for Highway Engineering, China People Transport Press, Beijing, China, 1993, in Chinese.

[33] Y. Fang, T. Lin, and S. L. Tan, Soil Mechanics, China University of Geosciences Press, Wuhan, China, 2003, in Chinese.

[34] B. Peng, J. A. Yuan, and J. L. Dai, “Research on stabilizer reinforced soil,” Journal of Xi’an Highway University, vol. 18, no. 3, pp. 229–234, 1998, in Chinese.

[35] S. Wang, Y. B. Zhang, and J. P. Zhuo, “Reactive mechanism of ISS stabilized soils and its application,” Highway, vol. 7, pp. 192–194, 2005, in Chinese.

[36] C. Dan and C. Z. He, “The effective factor of the potential distribution in diffused double layer,” Chemical Research and Application, vol. 10, no. 3, pp. 192–194, 1998, in Chinese.