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Assessment of recycled sulfur-free lignin as additive for sustainable soil improvement in geotechnical engineering with focus on frost resistance

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Abstract:

This study investigates using Sulfur-Free Lignin (SFL) as a stabilizer to improve and reinforce soil for civil engineering construction. To comprehensively evaluate the engineering performance of SFL stabilized soil, 3, 7, 10, 12 and 15% mixtures were used and the influence of climate factors (assessed subjecting the soil to different freeze-thaw cycles) was also considered. The experimental program investigated mechanical strength (unconfined compressive strength) and physicochemical properties, which included grain size distribution, Atterberg limits, variation of elemental and mineral composition, pH, cation exchange capacity, X-ray diffraction/ fluorescence and thermal conductivity. In addition, micro-characterization through SEM and pore size distribution was also covered. A considerable improvement of the mechanical properties was observed, which increases with SFL content up to 12%. This was based on changes in the physical and not chemical properties, hinting that the stabilization mechanism consists in physical binding unlike for traditional soil stabilizers. Moreover, it was found that SFL addition improved frost resistance. Based on these results, utilizing SFL as a soil stabilizer for application in earthworks shows great potential and would promote the bio-ethanol industry and engineering construction to be more sustainable and greener, particularly because it does not risk inducing soil pH contamination unlike traditional chemical agents.

Keywords: sulfur-free lignin, soil improvement, freeze-thaw cycles, sustainable geotechnical engineering, bioethanol waste elimination

1 Introduction

Ensuring the safety and reliability of earth structure such as foundations, embankment dams, canals and rail/road subgrade is one of the main concerns of geotechnical engineering (Jalili et al., 2018). Sometimes foundation soils display undesirable engineering properties and therefore stabilization may be required, e.g. by compaction or preloading, dewatering, electro-osmosis or addition of cementing agents, where the last are typically most convenient from the perspective of economic requirements and general applicability. However, traditional cementing agents such as lime, Portland cement or fly ash, have considerable drawbacks: (i) Clinker production for these traditional agents emits large CO₂ amounts and consumes huge energy. For example, typical manufacturing of 1 t Portland cement consumes 5000 MJ and releases about 0.95 t CO₂, contributing to about 4-5 % of global CO₂ emissions from fuel consumption and industrial activities (Xi et al., 2016; Shibab et al, 2018). (ii) The pH values of traditional treated soils have clear increasing trends, which lead to an alkaline environment posing a threat to the crop yield capacity and the quality of groundwater (Sreekrishnavilasam et al., 2007). (iii) Due to the excessively brittle performance, these treated soils may have an adverse effect on the stability of structures, especially under dynamic cyclic loads. Obviously, these problems cause a huge environmental burden and are incompatible with the global concept of sustainable development (Jefferis, 2008; Reddy and Kumar, 2019). Therefore, it is necessary to find innovative soil stabilizers, which are environment-friendly and energy-efficient, to enhance the geotechnical properties of problematic soils.

Lignin is the second most abundant biopolymer in the world after cellulose (Pérez et al., 2019). In nature, lignin polymer usually fills the space in the cell wall between cellulose, and hemicellulose, it forms xylem cells and lignifies sclerenchyma fibers, becoming the crucial structural part of the lignocellulose polymer (Martone et al., 2009). Until recently, lignin was mainly generated as a by-product from paper and timber industry. Today lignin is also a by-product or waste material of maize plant based ethanol production. Fig.1 shows the industrial

process of the maize plant ethanol production. Firstly, corn is peeled off as food, then the remaining corncob and maize straw are used as feedstock, which is converted to bioethanol through an environmental-friendly process of biological pretreatment and enzymatic degradation. The solid residue can be further processed to obtain multiple co-products including cellulose, hemicellulose and lignin. Cellulose is an important raw material for producing bioethanol. Hemicellulose, which is rich in five-carbon sugars xylose and arabinose and the six-carbon sugars mannose, can be used to produce xylitol gum, probiotics yoghurt or other high value products. However, lignin is predominantly used and investigated as a fuel (Hamelinck et al., 2005; Li et al., 2015), as it requires depolymerisation for other uses (Chio et al., 2019). For the biofuel industry to become truly sustainable, it is necessary to convert lignin into a high-value product (Bothast and Schlicher, 2005).

Fig.1. Industrial process of maize plant ethanol production

In the recent past, many studies have been implemented to assess the feasibility of utilizing lignin in the construction industry and in particular as an innovative agent to stabilize geomaterials. For example, lignin is being increasingly used as a reinforcement in composites due to its good thermal insulation properties (Alsina et al., 2005; Nechita and Ionescu, 2018). Furthermore, Peralta et al. (2012) suggested its use in the pavement industry as an asphalt modifier or substitute.

Surdahl et al. (2007) evaluated lignin as a stabilizer for silt roadways through a field test in south central Arizona and found it to be among the best performers in a group of six additives. Santoni et al. (2002) and Tingle and Santoni (2003) used lignin to treat silty and clayey soils, respectively, and found it to be more effective than traditional stabilizers in waterproofing, although unconfined compressive strength was better than traditional stabilizers for fine grained soils only. Similar conclusions regarding water resistance were reported by Ta'negonbadi and Noorzad (2017). Vinod et al. (2010) conducted experiments to assess the internal erosion

behavior of lignin-treated dispersive and erodible soils using a process simulation apparatus for internal crack erosion and found the erosion resistance of treated soil to have significantly improved. They also investigated and identified the mechanisms by which a remoulded expansive soil was modified by lignin (Alazigha et al., 2018). More recently, Zhang et al. (2017, 2018b) performed a series of laboratory and field tests to present a comprehensive investigation on engineering properties of lignin-stabilized silty soils and successfully employed nondestructive techniques (*i.e.* shear-wave velocity and thermal resistivity) to trace the evolution of strength for the lignin-stabilized soils.

This research demonstrates that lignin could indeed improve the geotechnical performance of soils increasing their mechanical strength and improving resistance to erosion and soil expansion. However, all of the mentioned studies investigated sulfite lignin (lignosulfonates) derived from paper industry, while the lignin obtained from ethanol production is sulfur free instead, which results in different properties. In particular, this contains more lignin (about 50-75%) with moderate macromolecular size and its structure is similar to that of native lignin. Limited studies have been carried out to examine the behavior of bioethanol-derived sulfur-free lignin to improve soils properties for civil engineering applications (e.g. Ceylan et al., 2012). As many engineering applications such as roads, railroads and pipelines are built in seasonally frozen regions, there is also a need to evaluate the performance of SFL stabilized soil under freeze-thaw conditions. Research has shown that freeze-thaw cycles severely affect the engineering properties of soils resulting in a clear decrease in soil stability (Simonsen and Isacsson, 2001; El-Maaty, 2016). In particular, Khoury and Zaman (2007) have reported that the durability of stabilized soils under repeated freeze-thaw action varies, depending on the type and proportion of stabilizer used.

As stated above, this study investigates the potential to use Sulfur-Free Lignin (SFL) based on a bioethanol industry by-product as a geotechnical stabilizer and highlights the performance of the stabilized soils considering climatic factors (with a high number of Freeze-Thaw cycles (F-T)). The physicochemical properties of the SFL stabilized soil under different F-T cycles were investigated, including Atterberg limits, Grain Size Distribution (GSD), Cation Exchange Capacity (CEC), pH and thermal conductivity. The elemental composition and crystal structure before and after freeze-thaw cycles were tested by X-ray Diffraction (XRD) and X-ray

Fluorescence (XRF). In addition, mechanical characterization was also performed by Unconfined Compressive Strength (UCS). Finally, the influence of F-T cycles on the stabilized soil at the microscopic level was confirmed by Mercury Intrusion Porosimetry (MIP) and Scanning Electron Microscopy (SEM).

2 Material tested

2.1 Soil

The soil tested was sampled approximately 40 cm underground from Qian'an in western Jilin Province, China. The site is located in Song-Nen Plain, one of the three largest soda saline-alkali soil areas (Wang, 1993). The physicochemical properties of the soil, including natural density and water content, Atterberg limits, optimum water content and maximum dry unit weight, total dissolved solids, organic matter content and pH are presented in Table 1. The particle-size distribution of the tested soil, measured by Laser Diffraction Particle Analyser (LDPA), is shown in Fig.3. It contains 18.5 % sand (2-0.075 mm), 52.4 % silt (0.075-0.005 mm) and 29.1% clay (<0.005 mm). According to the engineering classification standards (Chinese standard, 1999), the tested soil can be classified as a silty clay. Fig.4 shows the mineral composition of the soil used in this study as obtained from XRD analysis. This consists mostly of Quartz, Clay minerals, Plagioclase and Calcite.

Table 1
Basic properties of nature soil

Property	Characteristic
Soil natural density(g/cm^3)	1.909
Natural water content w (%)	21.58
liquid limit (%)	34.85
plasticity limit (%)	18.47
plasticity index (%)	16.49
Optimum moisture content (%)	15.6
Maximum dry unit weight(γ_{dmax}), (Kg/m^3)	1.781
Total dissolved solids (mmol/kg)	43.92
Organic matter content (%)	0.40
pH	8.7

Fig. 3. Grain size distribution of natural soil.

Fig. 4. Mineral composition of natural soil. (a) bulk sample and (b) clay fraction

2.2 Lignin

The Sulfur-Free Lignin (SLF) used is a recycled by-product from corn-based ethanol industry. Sulfur-free lignin from bio-ethanol industries is nontoxic, environmentally friendly and sustainable. This kind of lignin is a light-brown powder with a fragrance odour that is slightly soluble. According to the producer, it contains 91.2% lignin, 0.12% residual cellulose/hemicellulose, and 0.67% ash content. The infrared spectrum of sulfur-free lignin are

presented in Fig.5 as recorded by the Thermo Scientific Nicolet iS10 Fourier transform infrared spectrometer. It can be observed that different strong band identifications include hydroxyl group (3420 cm^{-1}), CH stretching vibrations ($2937, 2850\text{ cm}^{-1}$), C=O group (1703 and 1602 cm^{-1} , respectively), aromatic ring and C-H deformation (1513 and $1463, 1032\text{ cm}^{-1}$, respectively), and C-O stretching for methoxyl groups (1221 cm^{-1}). According to previous studies (Abe et al., 2010; Lin and Dence, 2012), lignin polymer is widely accepted to contain three major precursors: (1) coniferyl alcohol, (2) sinapyl alcohol and (3) p-coumaryl alcohol as shown in Fig. 5.

Fig. 5. FTIR spectrum of the sulfur-free lignin and three basic-units in lignin molecule (Lin and Dence, 2012).

3 Experimental procedure

3.1 Sample preparation

The natural soil collected was air-dried and lightly disaggregated with a rubber hammer to a particle size that could pass through a 2 mm sieve to remove any oversized particles for experiments. Subsequently, the SLF was added to the soil in amounts calculated on the basis of the soil dry mass and the designed additive contents (0, 3, 10, 12, 15%). To distribute the

additive uniformly, the mixture of SFL and soil was thoroughly mixed for about 5 minutes in a dry state. Afterwards, a predetermined weight of distilled water was added into the mixture. This was also hand-mixed for 5 minutes and then placed in a sealed metal bucket for 24 h to achieve a homogeneous moisture distribution. Note that the moisture content of all samples was the same as the optimum moisture content of the natural soil. Finally, the mixture was put into a hollow steel mold, having a 39.1 mm inner diameter and 80.0 mm height and compacted to 95% of the maximum dry density of the natural soil by using a hydraulic frame. Right after, the soil specimens were immediately sealed with a waterproof membrane and cured at $20 \pm 2^{\circ}\text{C}$ and relative humidity $92 \pm 3\%$ in a standard curing room for 28 days.

3.2 Testing methods

A series of experimental tests were performed including physical/chemical, mechanical and micro-characterization to investigate the changes in geotechnical properties of sulfur-free lignin stabilized soil undergoing a high number of Freeze-Thaw (F-T) cycle. The related damage mechanisms were then identified. The experimental program included Atterberg limits, Grain Size Distribution (GSD), Thermal Conductivity (TC), Cation Exchange Capacity (CEC), pH, X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Unconfined Compressive Strength (UCS), Mercury Intrusion Porosimetry (MIP) and Scanning Electron Microscopy (SEM). The experimental devices, techniques, and methodology adopted in this study are briefly described in the following paragraphs. Fig.2 illustrates a schematic overview of the testing program.

3.2.1 Freeze-thaw cycles

The sealed specimens underwent cyclic F-T cycles after 28 days curing in an automatic closed system, where no moisture was supplied or allowed to escape during the freeze-thaw process. The F-T cycles imposed cover a large range of values starting from the initial state (no cycle) and progressively 10, 30, 60, 120 cycles. In a single F-T cycle, the specimen was exposed to freezing condition at a temperature of -20°C for 12 h and then it was allowed to thaw at a room temperature of about 20°C for 12 h to ensure complete frost penetration and ice-melting, respectively. When the designed number of F-T cycles was achieved, the other tests were performed on this set of specimens.

3.2.2 Physicochemical tests

The Atterberg limits of all sulfur-free lignin stabilized soil specimens were measured and calculated in accordance with ASTM D4318-10 (ASTM, 2010). The grains size distribution was determined using a Laser Diffraction Particle Analyser (Bettersize BT-9300 LD) as described by Yang and Wei (2012). A DRE-2C thermal conductivity analyzer was used to measure the thermal properties of all specimens after targeted F-T cycles. This device utilizes transient plane source method with an accuracy of $0.1 \text{ W}/(\text{m} \cdot \text{K})$. Since the test temperature has an effect on the measured thermal conductivity, this was set to $15 \pm 0.5^\circ\text{C}$ for all specimens (Cheng et al., 2014). The ferric ammonium EDTA method was used to determine the Cation Exchange Capacity in accordance to the Chinese Standard (1999). The specimen pH was obtained by using a PB-10 probe (Sartorius Crop. Germany) as per ASTM D4972 (ASTM, 2007).

3.2.3 Mechanical tests

The unconfined compressive test, which is an effective method for strength evaluation, was carried out as per ASTM D4219 (ASTM, 2002) on cylindrical specimens having 39.1 mm diameter and 80 mm height. The ASTM standard recommends applying the axial load to produce axial strain at rate of approximately 1.0 mm/min for ductile materials and 0.3 mm/min for brittle materials. In order to test all mixtures under similar conditions, as well as to isolate the effect of strain rate on strength behavior, a constant displacement rate of 1.0 mm/min was applied in a YSH-2 Soil Unconfining Pressure Test Apparatus (Nanjing Soil Instrument, China). The unconfined compressive strength was defined as the peak value in the stress-strain curve as shown in Fig. x. Since the height-diameter ratio (H/D) of a specimen has an effect on the compressive strength (Lamond and Pielert, 2006), it should be noted that the ratio used was 2.05.

Fig. x. Using peak strength of stress-strain curve as unconfined compressive strength.

3.2.4 Elemental and mineral composition tests

The crystallographic structure of the stabilized soil was investigated using an X-ray diffractometer (D/MAX-2500, Rigaku, Japan) with a Cu-K α radiation source at a voltage of 30 KV. The scanning speed was 6° (2 θ)/min over an angle range of 2.6 ° to 45°. The “K-value” method was used for XRD quantitative analysis in accordance to SY/T 5163-2010 Standard (Chinese Standard, 2010a). X-ray fluorescence tests were also carried out to determine the elemental composition of the specimen. The tube-above wavelength dispersive X-ray fluorescence spectrometer (ZSX Primus II, Rigaku, Japan) was used as per GB/T 14506 Standard (Chinese Standard, 2010b). The quantitative data analysis was performed with the bundled EZ-scan software.

3.2.5 Micro-characterization tests

The pore size characteristics of the treated soil were analysed using the Mercury Intrusion Porosimetry (MIP) technique. In this technique, mercury intrudes the voids of the porous medium only if sufficient pressure is applied. The intrusion pressure is then converted to the pore diameter according to Laplace’s capillarity law also known as Washbur’s equation (Washburn, 1921). Cubic specimens (about 10 mm length), which were sub-sampled from each compacted specimen, were freeze-dried immediately before MIP testing as suggested by Delage (1984) to avoid fabric alteration. The MIP device used was the AUTO-PORE 9500 (Micromeritics Instrument Corp. America) with a maximum intrusion pressure of 228 MPa. Scanning Electron Microscopy (SEM) was also conducted to more directly observe the spatial configuration (i.e. sizes, shapes and associated pores) of sulfur-free lignin stabilized soil

226 particles. The technique provides qualitative information that can be interpreted along with MIP
227 test results. The SEM specimens were also pretreated following the same procedures as for MIP.
228 In addition, the specimens were sputter-coated with a thin gold layer before SEM testing. The
229 images were taken with a Phenom ProX Desktop scanning electron microscope (Thermo Fisher
230 Scientific, America).

231

Fig. 2. Schematic overview of the work performed in this study.

4 Results and discussion

4.1 Physicochemical tests

4.1.1 Atterberg limits

The liquid limit (w_L) defines the water content where the soil behavior transitions from a plastic state to that of a viscous liquid, while the plastic limit (w_P) defines the water content where a soil transitions from a semi-solid to a plastic state. These water contents define the limits within which the soil is workable and are termed after Atterberg who first defined them. Fig.6 shows the influence of SFL content and F-T cycles on liquid limit (w_L), plastic limit (w_P) and plastic index ($I_P = w_L - w_P$). It can be observed in Fig. 6 (a) that w_L and w_P increase approximately 18% and 14% respectively when the SFL content changes from 0% to 15%, resulting in a considerable increase in I_P of 24%. These results are consistent with those on silt soils stabilized with lignosulfonate presented by Zhang et al. (2018c). The increase in w_L and w_P is thought to be due to soil particles being bonded by the lignin fibers, resulting in a more stable soil structure. Consequently, more water is required to complete state transitions. The low solubility of SFL, which leads to strong-holding capacity in the stabilized soil, may also explain these results. The results are consistent with those on silt soils stabilized with lignosulfonate presented by Zhang et al. (2018c).

With respect to the F-T cycles effects on I_P there is no clear trend, as shown in Fig. 6(b), implying that F-T cycles have little influence on Atterberg limits. This result is also consistent with former studies (Eigernbrod 1996, Liu et al., 2019). Dagesse (2015) saw no effect of freezing and thawing on soil plasticity based on indoor experimental data, but he pointed out that the small samples used to measure liquid and plastic limits would reflect small scale changes and this might have a significant effect during project designing.

Fig. 6. Variations of Atterberg limits of different sulfur-free lignin content with different F-T cycles.

4.1.2 Grain size distribution

Fig.7 displays the variation in grain size distribution of the stabilized soil for different SFL contents that underwent different F-T cycles. The sand percentage of the stabilized soil has an increasing trend with addition of SFL up to 7%, and then starts to decrease. The amount follows

an opposite trend than for the silt group, where a smaller percentage was apparent in the 7% SFL stabilized soils. However, the percentage of clay keeps on decreasing as the SFL content increase. In order to better analyse the causes of grain size changes, the pure SFL powder was also tested using the same method. This contains 15% clay-size particles ($<0.005 \mu m$), 79% silt particles ($0.005-0.075 \mu m$) and about 6% sand-size particles ($>0.075 \mu m$). These results indicate that SFL could convert significantly fine particles into coarse particles by aggregating or cementing them up to 7% SFL content, afterwards, the relative amount of the coarse particles gradually decreases because SFL contains almost 80% particles belonging to the silt group. However, this does not necessarily mean that the cementing process stops or weakens.

In Fig. 7, it is also seen that the F-T cycles have a significant effect. The sand percentage of all specimens shows a decreasing trend in Fig. 7(a). The sand percentage of the untreated soil and the low content SFL stabilized soil rapidly decreases by approximately 5% during the first 60 cycles, while the high SFL content stabilized soil has a slight decrease throughout the F-T process. The silt percentage also shows a decrease except for the natural soil and the 3% SFL stabilized soil. Consequently, the clay percentage increases with the F-T cycles, and similarly the most changes are found in natural and low dosage specimens in Fig.7 (c).

Fig. 7. Relationship between Sulfur-free lignin content and grain size composition of stabilized soil under different F-T cycles: (a) sand group (2–0.075 mm); (b) silt group (0.075–0.005 mm); (c) clay group (< 0.005 mm).

According to the test results described, the redistribution of soil particles size indicates that SFL plays a role in bonding soil particles, while F-T cycles have opposite effects, breaking up coarse particles to enrich the fine group. However, the SFL stabilized soil undergoes less changes during F-T cycles, which agrees with studies by Russo et al. (2007) who also conducted F-T cycles on different soils. In addition, the results confirm intense fragmentation of particles at the beginning of the F-T cycling process and gradual decrease subsequently, as already observed by Zhang et al. (2016). Numerous studies have been examined the effects of F-T cycles on grain size distribution of soil. According to Konichev (1981), sand particles are fragmented as a result of the freezing thawing process and the grading tends towards a certain particle size and degree of the fragmentation in relation to its initial particle size distribution. Furthermore, according to Bullock et al. (1988), the F-T cycles destroy bonds that hold aggregates together, leading to a variation in soil particle size distribution.

4.1.3 pH & CEC

Fig.8 reports the pH variations for different SFL stabilized soils that underwent 30 and 120 F-T cycles. The pH of the SFL stabilized soil has a slight decrease with SFL content but remains comparable with the natural soil, meaning SFL does not change significantly the pH of soils. This result is different from previous studies that report strongly alkaline pH after treatment with lignosulfonate obtained from paper industry (Lisperguer et al., 2009; Zhang, 2015), cement (Chew et al., 2004) or lime (Sharma et al., 2012). Compared with traditional chemical stabilizer (*i.e.* lime, cement, fly ash) and lignosulfonate, this is a clear advantage of SFL. It also can be seen from Fig.8 that the F-T cycles have no significant influence on pH for all soil specimens, due to testing in a closed environment.

Fig.9 shows an increase in CEC, as more SFL is added. Using the 10% and 15% SFL stabilized soil as an example, the CEC grows by 6.7 and 18.1 mmol/100g in the condition of no F-T cycles. This is attributed to SFL being separated from cellulosic feedstock (corn cobs and corn stover) using steam explosion followed by alkaline (NaOH) addition during the pretreatment of bioethanol production, after which acid is added to neutralize the pH values. However the Na⁺, which possesses a strongly exchangeable ability, remains in SFL causing an

308 increase in CEC. According to Tang (1998), high CEC causes the loosely bound water layer on
 309 the clay particles to become thicker, resulting in soil instability. Frenkel et al. (1978) reported
 310 that the increasing exchangeable sodium percentage enhances soil dispersion, especially the
 311 maximum dispersion occurred at pH 8.3. Thus, SFL should be used with more caution when
 312 treating dispersive soils or mixing with other materials in engineering applications. Furthermore,
 313 there are no marked changes in CEC for all specimens before and after F-T cycles similarly to
 314 the pH tests.

Fig. 8. Variations of pH for different sulfur-free lignin content with different F-T cycles.

Fig. 9. Variations of cation exchange capacity for different sulfur-free lignin contents with different F-T cycles.

4.1.4 Thermal conductivity

The thermal conductivity of specimens decreases as the SFL content increases, reducing from 1.55 to 1.19W/(m•K) before any F-T cycle, as shown in Fig.10. As a natural organic polymer, lignin has excellent heat insulation capacity. Its thermal conductivity ranges from approximately 0.1 to 0.5 W/(m•K) for different plants (i.e. softwood, cotton, ramie) (Gupta et al., 2003; Yapici et al., 2011), which is lower than that of soils and explains the behavior in Fig. 10.

Fig. 10. Variations of thermal conductivity for different sulfur-free lignin contents with different F-T cycles.

Fig.10 also illustrates that the thermal conductivity of all specimens tends to decrease with increasing F-T cycles. This result is consistent with previous studies about the effects of F-T on soil or concrete thermal conductivity (Pan et al., 2017; Zhang et al., 2018a). Li et al. (2019) and Moghbel et al. (2018) considered that during the freezing process, the free water transitions from liquid to solid ice lens, increasing the soil pore size or leading to crack formation in the soil matrix. Hence, these larger pore size and gaps behave as an isolator in the heat-transfer process, thereby reducing the thermal conductivity of the stabilized soil. Furthermore, Al Nakshabandi and Kohnke (1965) already claimed that thermal conductivity is correlated to the grain size distribution, and Abu-Hamdeh and Reeder (2000) specifically reported that thermal conductivity decreases as finer particles increase. The grain-size distribution results discussed earlier also support this claim. Finally, it can also be seen that the reduction is steeper for the natural soil than for the SFL stabilized soil, especially during the first 30 F-T cycles, which indicates that the stabilized soil has better frost resistance.

340 4.2.1 Unconfined compressive strength test

341 Fig.11(a) illustrates the Unconfined Compressive Strength (UCS) of the SFL stabilized
342 soil undergoing different F-T cycles. It is observed that the compressive strength (q_u) of the
343 specimens initially increases and then reduces as the SFL content increases. The maximum q_u
344 was found at 10% content, reaching 1159 kPa, which is close to the strength at 12% SFL
345 content (1066 kPa). The UCS strength of 10% stabilized soil increases about 500% after 28
346 days curing compared with that of the untreated soil, which means SFL is quite efficient in
347 improving strength. Yang et al (2018) used lignin to treat clayed sand, sandy silt with clay and
348 sandy silt and found that the UCS increased up to 300, 370 and 500% respectively after 28-
349 days curing. These results support the UCS performances obtained from this paper. Based on
350 the grain size distribution results, it appears that the decrease in q_u when the SFL content
351 increases beyond 10% may be ascribed to excessive SFL, which prevents bonding between soil
352 particles. This suggests that the optimum SFL content for improving and enhancing the silt clay
353 soil in Jilin Province is between 10% and 12%. It is also noteworthy that UCS clearly drops
354 during the first 10 F-T cycles for all soil samples. However, the UCS of high SFL content
355 stabilized soil shows a considerable decrease up to 60 F-T cycles reaching about 480 kPa.
356 Similar trends were reported by Kravchenko et al. (2018) and Li et al. (2013), who used fibers
357 to improve clay soils and silt soils. The F-T cycle is considered as a process of dynamic
358 equilibrium where the formation and melting of ice gradually leads to a relative stable soil
359 structure (Lee et al., 1995; Zhang et al., 2015b). In other words, more F-T cycles are required
360 to reach a new balance in a stable soil structure compared to a loose soil matrix. Wang et al.
361 (2007) thought the internal fabric of fine-grained soil usually reaches to a new dynamic balance
362 when the soil has been exposed to 6 – 10 F-T cycles. This suggests that the SFL stabilized soil
363 has better frost resistance and the untreated soil is almost completely lost strength once it is
364 exposed to F-T cycles.

Fig. 11. (a) Variations of unconfined compressive strength for different sulfur-free lignin contents with different F-T cycles (b) Variations of unconfined compressive strength decrease rate with different F-T cycles.

In order to better analyze the frost resistance of the soil specimens, Fig.11 (b) presents the variation of UCS decrease rate under different F-T cycles, which is expressed as

$$SDR_n = \frac{q_{un} - q_{u0}}{q_{u0}}$$

Where SDR_n is the UCS decrease rate of the soil specimens after n F-T cycles, q_{un} is the strength value after n F-T cycles and q_{u0} is the strength of the specimens after 28 days curing before undergoing any F-T cycles. It can be seen that the UCS decrease for the untreated soil is approximately 65% during the first 10 cycles and ultimately reaches about 74%. As the amount of SFL increases, the performance to frost resistance is better under few F-T cycles. For instance, the strength of 15% stabilized soil only decreases about 26% and 33%, respectively, after 10 and 30 F-T cycles, which is a significant improvement in terms of frost resistance. The difference in SDR_n for 10% and 12% SFL stabilized soil, which is about 60% and 65%, respectively, is not apparent after 60 and 120 cycles. Moreover, the 15% SFL stabilized soil shows the best frost resistance under high F-T cycles, with the lowest strength reduction rate of 46% and 57% related to 60 and 120 cycles. Although less strength reduction is observed in the natural soil or low SFL content stabilized soil, the absolute UCS value after reduction is overall higher for high SFL contents. These results may be attributed to the relatively heavy molecular mass of lignin, making it more stable, just like its supporting and strengthening function in the cell wall of plants (Gandini and Belgacem, 2008). According to the above results, SFL could effectively improve the frost resistance of soils.

4.3 Elemental and mineral composition

4.3.1 X-ray Diffraction analysis

Fig.12 shows the X-Ray Diffraction (XRD) patterns of the natural soil and 15% SFL stabilized soil with no F-T cycles and 120 cycles. As lignin is an amorphous material (Han et al., 2019) and therefore it is not responsive to XRD testing, comparison of the diffraction peak patterns for the untreated soil and the SFL stabilized soil shows that no new mineral is formed by chemical reactions, as they are almost identical. This is opposite to the results from Modarres et al (2015) and Amini et al (2019), who used lime and cement to improve soil, respectively. There, new diffraction peaks for hydrated calcium silicate (CSH) and hydrated calcium aluminates (CAH) were found in the stabilized soil. Nonetheless, there is still a noticeable difference in the peak intensity of the stabilized soil, which has a slightly decrease compared to the untreated soil. Alazigha et al (2018) observed the same phenomenon when using

lignosulfonate to improve expansive soil and thought this may be due to the amorphous properties of lignin restricting diffraction of mineral atomic planes. The same main minerals were detected and identified in all soil specimens and include Quartz, Plagioclase, Calcite, Illite and Illite/Smectite mixed layer, as indicated in Fig.12. Furthermore, no change can be observed before and after 120 F-T cycles indicating that F-T cycles cannot dissolve the minerals. This is consistent with results by Zhao et al. (2019). Based on XRD results, SFL does not strengthen the soil through chemical reaction to generate new composition unlike lime or MgO.

Fig. 12. XRD diffraction patterns of natural soil and 15% SFL stabilized soil under 0 F-T cycles and 120 F-T cycles (Pl: plagioclase; P: potassium feldspar; C: calcite; H: hornblende; It: illite; K: kaolinite; Q: quartz; I/S: illite/ smectite mixed layer).

4.3.2 X-ray Fluorescence analysis

The elemental composition of the same four soil specimens were also examined through X-Ray Fluorescence tests (XRF) to confirm whether adding SFL would mix in other inorganic elemental compositions. The results are presented in Table. 3. It is clear that no heavy metal elements (such as chromium, nickel and cobalt) or sulfur element were detected, meaning that utilizing SFL- based bioethanol industrial by-product as a geotechnical material to strengthen soil and meet engineering requirements would not cause environmental contamination issues.

After adding SFL, the amount of silicon dioxide is the element changing the most and it reduces by about 10%. Accordingly, loss on ignition (LOI) increases by about 12%. This is due to the fact that after 950°C ignition, lignin turns into organic carbon, leading to a significant increase in the relative amount of LOI and relative reduction of other elements. At the same time, it can also be found that there are no variations in the specimens under different F-T cycles, indicating F-T has no effects on elemental composition, consistently with the XRD results.

Table 3

The elemental composition of 0% and 15% SFL stabilized with no and high F-T cycles

Sample ID	Composition (%)												
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	P ₂ O ₅	MnO	LOI	Total
0% SFL F-T 0	66.27	11.55	2.51	0.40	5.04	1.69	2.88	2.57	0.50	0.07	0.07	6.33	99.90
0% SFL F-T 120	68.07	11.23	2.15	0.43	4.55	1.58	2.93	2.62	0.48	0.07	0.06	5.73	99.92
15% SFL F-T 0	57.81	10.60	2.77	0.04	4.69	1.54	2.57	2.33	0.46	0.07	0.07	16.58	99.53
15% SFL F-T 120	56.60	10.85	2.94	0.04	4.95	1.53	2.54	2.19	0.46	0.06	0.07	17.49	99.74

Note: LOI means value of loss on 950°C ignition.

4.4 Micro-characterization test

4.4.1 Mercury intrusion porosimetry test

Fig.13 (a) illustrates the variations of pore size distribution with SFL content before undergoing any F-T cycles. The total mercury intrusion volume gradually decreased from 0.159 to 0.142 mL/g, with SFL content increasing up to 15%. Upon further analysis, it can be seen that the mercury volume of macropores (4 – 40 μm) and mesopores (0.4 - 4 μm) showed a decreasing and increasing trend, respectively, after 3% SFL addition. When SFL reaches 15%, the volume of both macropores and mesopores clearly reduced. This means that SFL first fills the macropores and then diminishes the mesopores, resulting in lower porosity for the stabilized soil. The same result was reported by Zhang et al. (2015) who tested the pore-size distribution of lignosulfonate stabilized silt soil. In addition, it can also be easily observed that there is a transformation in the differential pore size distribution from bimodal for the natural soil to unimodal for high content SFL stabilized soils. For the natural specimen, two dominant pores

433 can be observed around 0.02- 0.04 μm diameters and 5 -7 μm diameters. For both 10% and
434 15% SFL stabilized soil, the peak in the differential pore volume relative to the smaller size
435 essentially disappears and the macropores shift to the left compared with that of the natural soil.
436 Zhang et al. (2015) also found soil that the soil pore structure of lignosulfonate stabilized silt
437 soil changed from bimodal for the natural soil and 2% content to a smooth unimodal distribution
438 for 8% and 12% specimens. Furthermore, it is worth noting that the 10% SFL stabilized soil,
439 which has dominant pore size diameter around 1 -2 μm , shifts left more than the 15%
440 stabilized soil. This is consistent with the UCS result that the 10% SFL stabilized soil has better
441 strength performance than the 15% SFL stabilized soil due to denser structure.

442 Fig.13 (b) shows the pore size distribution of the natural soil and 15% stabilized soil after
443 120 F-T cycles. The F-T process increases distinctly the cumulative intrusion of mercury in the
444 natural soil from 0.159 to 0.192 mL/g. However, the variation is about half (0.012 mL/g) for
445 the 15% SFL stabilized soil. Moreover, the dominant macropore size of the natural soil shows
446 an evident shift to the right from 6 to 9 μm , while there is negligible change in the curve for
447 the 15% SFL specimen. The reason for increasing porosity and dominant pore size is mainly
448 because the free water in the soil pores expands about nine-percent during the freezing process
449 leading to permanent changes in the pore-size distribution characteristics (Konrad, 1989). At
450 the same time, these results are consistent with the thermal conductivity and UCS tests and
451 prove that SFL could effectively improve the frost resistance of the stabilized soil.

Fig. 13. (a) Mercury intrusion porosimetry results for different SFL contents after 28 days curing without F-T cycles; (b) Mercury intrusion porosimetry results for natural soil and 15% SFL stabilized soil with no and 120 F-T cycles.

4.4.2 Scanning electron microscopy (SEM)

The SEM images of the natural soil and the SFL stabilized soil with different F-T cycles are presented in Fig.14 (500-1000 times magnified). Comparing Fig.14 (a) and (b), it is easy to

456 see that the soil particles of the natural soil are connected with each other mainly by point
457 contact, without any cementing, while the soil particles are coated and bonded by adhesive
458 material formed after mixing SFL. Moreover, the natural soil shows a looser structure with
459 more pores in contrast with a denser and hence more stable structure for the stabilized soil, due
460 to more aggregated soil particles. Fig.14 (c) also shows that small soil particles agglomerate
461 together to form large particles. Through magnifying a detail (Fig. 14(d)), it can be seen that
462 the individual soil particles are coated with natural polymer that binds the particles together.
463 Combining the above to XRD, XRF, and CEC results, it appears that the SFL stabilizes the soil
464 by physically bonding the soil particles together. The bonding could be ascribed to electrostatic
465 attraction between sulfur-free lignin and soil minerals, as proposed by Tingle et al. (2007) and
466 Vinod et al. (2010). Fig.14 (c) and Fig.14 (d) show that F-T has undesirable effects on the
467 solidified soil matrix, accounting for the looser soil structure. Furthermore, several
468 microfractures are generated on the surface of natural soil particles, which indicates the soil
469 particles started to break into smaller ones (Fig.14 (e)). Some researchers (Poltev, 1968; Zhang
470 et al. 2016) suggested that the phase change of free water (from liquid to solid phase) generates
471 micro-cracks on the surface of soil particles by temperature tension and then these micro-cracks
472 are filled by water film and sustainably develop into macro-cracks (width about 10 μ m) with
473 increasing number of F-T cycles. ~~and The cracks, which may be caused by cyclic frost heave~~
474 ~~forces during the F-T process, were found both in the fine soil matrix and the coarse particles~~
475 ~~of the stabilized soils.~~ As a result, these macro-cracks crushed the coarse particles and resulted
476 in a scattered structure in the SFL treated soil as shown in Fig. 14 (f). The macro-cracks induced
477 by F-T cycles at aggregates scale were also observed by Olgun (2013) and Liu et al. (2019).
478

Fig. 14 Scanning electron microscopy images of the natural soil and the SFL stabilized soil without and with 120 F-T cycles: (a) natural soil and no F-T cycles; (b) 15% SFL stabilized soil after 28 days curing and no F-T cycles; (c) 15% SFL stabilized soil after 7 days curing and 120 F-T cycles ($\times 500$); (d) 15% SFL stabilized soil after 7 days curing and 120 F-T cycles ($\times 1000$); (e) natural soil and 120 F-T cycles; (f) 15% SFL stabilized soil after 28 days curing and 120 F-T cycles .

5 Conclusions and limitations

This paper shows the use of Sulfur-Free Lignin (SFL) to stabilize soil for earth works. The geotechnical properties of stabilized soil-SFL mixtures were comprehensively investigated from a physicochemical, mechanical, elemental and mineral composition point of view, interpreting the results from a micro-mechanical perspective. A considerable improvement in uniaxial compression strength was observed, which increase with SFL content up to 12%. The physical properties also changed, but not the chemical ones. Therefore, the stabilization mechanism consists in physical binding unlike for traditional soil stabilizers. Moreover, the stabilization and damage mechanisms under climatic factors (Freeze-Thaw cycling) were also investigated and it was found that SFL addition improved frost resistance. In particular, according to the results:

- The consistency limits increased slightly when adding SFL, while the coarse soil particles (sand and silt groups) exhibited a significant increase.
- The use of NaOH in the production process of bioethanol leads to a considerable CEC increase in the SFL stabilized soil. However, the pH was unchanged regardless of the SFL% added.
- After curing 28 days, the unconfined compressive strength increased about 5 times (230 to 1158kPa) for the 10% SFL stabilized soil, which is around to the optimum SFL dosage.
- With increasing SFL content the porosity fabric changed from bimodal to unimodal and the total pore volume decreased, but no new mineral was formed nor change in elemental composition. The stabilization mechanism therefore consists in physical binding such as coating finer soil particles, bonding isolated particles and filling intra-aggregate pores unlike traditional soil stabilizers.
- The frost resistance showed a considerable improvement with increasing SFL content. Even if UCS reduced with F-T cycles, due to physical damage (such as crushing of coarse particles and cracking of the fine soil matrix), it remained 7 times higher for the SFL treated soil even after 120 cycles. Furthermore, adding SFL increases the thermal insulating properties of the treated soil improving frost resistance.

Based on these experimental results, SFL shows great potential as a novel stabilizer to

improve the engineering behavior of soil and offers an alternative to traditional chemical agents, particularly because it does not risk inducing soil pH contamination. However, SFL should be used cautiously to treat dispersive soils due to increased CEC. Further work should address climate factors under dry-wet cycles and the dynamic behavior should be evaluated in relation to the use of SFL-stabilized soils as road substrates are subjected to traffic loading.

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