Swelling suppression of black cotton soil by means of liquid immersion and surface modification

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ABSTRACT

Although the surface organic modification of smectite has been investigated widely, the swelling behavior of clays has been scarcely studied with consideration of civil engineering applications. In this work a facile strategy of liquid-immersion (dilute H2SO4 aqueous solution) was proposed, and the 3-aminopropyltrimethoxysilane (APS) was utilized as surface modifier to suppress expansibility of black cotton soil (BCS) which is a type of highly swelling soils in tropical areas. Factors such as the incorporation dosage of APS, surface characters of soil treated by solution of H2SO4 or Na2CO3, and reaction temperatures/time were investigated to get lower swelling ratios. The treatment of BCS by H2SO4 was found more effective in immobilizing APS molecules, and hydronium ions were suppressed after the APS modification. The free swelling index (FSI) of BCS was decreased from 120% to 15% after treatment with H2SO4 and appropriate amount of APS modification. The reaction can be completed within several hours at the room temperature to ~80°C. The soil samples were characterized by different means including the X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electron microscope, thermogravimetric analysis and Zeta potential measurements. The APS molecules were found to react with –OH groups of the clay, and the hydrophobic groups provide surface hydrophobicity, which prevents hydration of cations within clay minerals. The APS was indicated to re-constructed lamellar structures of smectites after H2SO4 treatment, which suppressed the intra-crystalline and the subsequent osmotic swelling. This research highlights the liquid immersion and surface modification is applicable in diminishing swelling ratios of highly expansive black cotton soil.

1. Introduction

Black cotton soil (BCS) is a type of highly expansive soils that are widely discovered in tropical areas, e.g., mid-south Africa, south-Asia, Australia, and some parts of China. The swelling/shrinkage behavior changed with moisture gives rise to serious problem in civil engineering, e.g. highly volumetric change, weakness in strength, and low bearing capacity (Gadre and Chandrasekaran, 1994; Uppal et al., 1970). It was reported that the economic losses is ca. $2.3 billion due to damages/disasters caused by swelling soils in forms of house/buildings cracking, subgrade/dam collapse, and pipelines destruction (Jones and Holtz, 1973; Kumar and Sharma, 2004). Although these disasters can be avoided by out-digging and replacing with concrete materials, yet the huge cost of earth removal is unacceptable. Sometimes the strategy of out-digging/replacing is impossible in case of remote region where only expansive soils can be obtained. For example, the BCS found in Kenya was discovered to occupy ~60% areas of the country. The savanna climate in Kenya provides periodical alternating dry/rainy seasons, i.e., BCS experiences two cycles of swelling/shrinkage annually. To suppress this expansive BCS as well as find a facile strategy to stabilize BCS without digging them out is an urgent task in the civil engineering. In a previous report, a strategy was developed to stabilize BCS via method of geopolymerization by adding Ca(OH)2 or KOH (Miao et al., 2017). However, the huge amount of earth excavation and solid crushing/mixing would make this means unavoidable in incorporating solid forms of alkali into BCS. Therefore, it is necessary to find facile means of liquid treatment or surface modification without excavation or digging.
soils out in order to simplify the practical engineering (Fattah and Al-Lami, 2016; Fattah et al., 2017).

The swelling property of BCS was found to originate from clay minerals of smectite group. Smectites are one of the most common minerals which have a 2:1 structures composed with aluminosilicate layers and exchangeable, hydrated cations in the interlayer (Romanzini et al., 2015). Presently the swelling of hydrated clays was known to have two reasons. The first is intra-crystalline swelling that always exhibits as a larger unit parameter in the direction of ‘c’ after interlayer cations were hydrated. Reasons of this swelling lie in weak forces of van der Waals interactions between interlayers of the clay mineral (e.g., montmorillonite) due to the presence of hydronium ions (Norrish, 1954). Although this swelling contributes minor expansion of the volume, the intra-crystalline swelling would induce the second step of swelling termed as osmotic swelling which contributes to larger volume expansion. In the osmotic swelling step there is always a liquid layer at the interface when more water was adsorbed. The osmotic hydration makes clay sheets more prone to slip from each other. Sometimes the clay were delaminated into separated sheets (Sasaki and Watanabe, 1998). The volume of clay/water was thus extremely enlarged. To decrease the expansion, strategies have been proposed by incorporation of lime, cement, slags, fly ash and thereof (Miao et al., 2017). The surface properties of clays are also found to have great influence on the swelling (McCarthy et al., 2016; Ozá and Gundaliya, 2013; Zhang and Cao, 2002). It was known that the surface hydrophobicity prevents clay particles from hydration, and the osmotic swelling can be avoided (Guo et al., 2014). The surface modification of clay minerals has attracted much attention because the clay composite exhibits special characters suitable for many applications (He et al., 2013). Herein, the BCS was tested to diminish swelling that were treated with liquid immersion (dilute H2SO4) followed by surface modification of 3-aminopropyltrimethoxysilane (APS), and factors such as incorporation dosages of APS, surface characters of BCS treated by H2SO4 or Na2CO3, and reaction time at different temperatures were investigated. Although the use of APS in modification of clay minerals was commonly found in literatures (Kotal and Bhowmick, 2015; Kurihara et al., 1996; Mishra et al., 2011; Wieczorek et al., 2016), the purpose of decreasing swelling ratios were scarcely reported in the civil engineering applications up to date. By means of this developed liquid-immersion and surface modification the swelling of BCS was suppressed, and the free swelling index was decreased from 120% to 15%.

2. Experimental work

2.1. Black cotton soil

The BCS was collected from a subgrade site (36°31′ E, 1°35′S, 1.5 m in-depth), south of Nairobi, Kenya, where a city loop road is to be constructed by China Road and Bridge Co. The chemical compositions were listed in Table 1, and the X-ray diffraction (XRD) pattern was depicted in Figure 1. Major mineral phases were found as smectite, feldspar and quartz. The basal diffraction peak exhibits a broad manner, and the first diffraction of pristine BCS was found at 2θ = 6.23° corresponding to d = 1.48 nm, which was the typical characteristic of hydrated smectites. The content of clay minerals including smectite, nontronite, chlorite and interstratified chlorite/smectite was evaluated to be 81.6% (Miao et al., 2018). The colloid index of BCS was determined to be 47.6 mL/15 g according to the means of Dakshamanurthy and Raman (1973), and this illustrates that the BCS comprises mainly with clay minerals. The amount of blue absorption was 33 mmol/100 g, and the cation exchange capacity (CEC) is 84.3 meq/100 g which were determined by the adsorption of methylene blue and copper bisethylenediamine methods (Miao et al., 2006).

2.2. Procedures of liquid-immersion and surface modification

In the first step a certain amount (e.g., 100 g) of pristine BCS (P-BCS) was added into the diluted H2SO4 solutions (100 mL) of different concentrations (2.5%–10%, wt.), and the slurry was stirred for 4 h. The H2SO4-treated soil was filtrated and rinsed with distilled water for three times. The collected product was dried at 105°C for 24 h. This sample was named as H-BCS. For comparison, the BCS soil was also treated by alkaline solution. Another portion of P-BCS was treated in the 8% wt. Na2CO3 solution via similar procedures, and the sample was named as N-BCS. In the second step, a desired amount (vs. CEC of BCS) of APS was dissolved in solution of ethanol/water (9:1 by volume, 100 mL), and a little portion of acetic acid was added to get the pH of 4–5. The APS/ethanol/water was then stirred for 1 h at room temperature. To modify the BCS, a portion of soil sample (P-BCS, H-BCS or N-BCS) was added to the solution of pH = 4–5 APS/ethanol/water, and the suspension was stirred for different periods (2, 4, 8, 12 h) at a certain temperature. Products were washed by distilled water till to the neutral pH, and were dried for 12 h at the temperature of 105°C. The modified soil samples were termed as N-Si-BCS and H-Si-BCS, respectively. The preparative procedures and characterizations were illustrated in Figure 2a, and the mechanism for BCS reacting with silane (APS) is indicated in Figure 2b.

2.3. Free swell index (FSI) measurements

The FSI is used to identify expansive clays and predict the swelling potentials. The FSI measurements were recorded on a free expansion instrument (WX-2000) according to standard methods (JTC E40-2007). Prior to this measurement, the soil samples were oven-dried after passing through a 425 μm sieve. A volume of 10 mL BCS powders were placed in a 100 mL graduated cylinder filled with 50–60 mL of water and 5 mL

![Figure 1. XRD pattern of the pristine BCS and indexed phases of major minerals (montmorillonite, quartz and albite).](image-url)
NaCl solution (5% wt.) to get a homogeneous dispersion. More water was filled in the graduated cylinder up to 100 mL. The soil-water mix was allowed to swell at room temperature. The swollen volume was recorded after 5 min, 10 min, 20 min, 30 min, 1 h, 2 h, and 3 h until the FSI value becomes constant. Measurements were triplicated to achieve a reasonable degree of accuracy (±5%). The value of FSI was calculated according to the equation (Golait and Kishore, 1990): FSI = (Vf−Vs)/Vs × 100%,
where the FSI denotes the volume of pristine BCS placed in cylinder.
and the Vs denotes the volume of swelled BCS in cylinder.

2.4. Unconfined compressive strength (UCS) measurements

The UCS is to evaluate mechanical properties of the expansive clays, which was conducted in accordance with ASTM D 2166 (ASTM, 2000). Typically, the unconfined compression tests were carried out on cylindrical specimens of 38.1 mm in diameter and 76.2 mm in length. The BCS and the modified soil were compacted at the optimum moisture content (OMC = 25%) in standard molds, and the OMC was obtained in our previous study (Miao et al., 2017). The compacted samples were kept in polyethylene bags in glass desiccator, and stored in a humidity chamber at constant temperature (25 ± 2 °C) for curing. After curing (different periods 0–90 days) samples were taken out of the mold, and used for the UCS tests. Tests (three parallel specimens) were recorded to get UCS values till failure or 20% strain, and the loading rate is set at a 1.2 mm/min. The maximum stress was obtained after the stress was plotted against strain.

3. Results and discussion

3.1. Free swelling index of BCS

The FSI values were listed in Table 2 to show the liquid-immersed BCS (e.g., H-BCS) with different concentrations of H2SO4 (2.5%–10%). The FSI measurements were conducted at different durations (0–8 h). The FSI was found to decrease with increasing concentrations of H2SO4 and prolonged reaction time. When the concentration of H2SO4 was 2.5%–7.5%, the decrement of FSI is more prominent. As the concentration of H2SO4 increases, e.g., 10%, the FSI decrement is less pronounced. In view of obtaining the least FSI, a concentration of 7.5% sulfuric acid solution and 4 h were chosen as the reaction parameters for H2SO4 treated samples. Reasons for diminishing the FSI can be found as clay structures destroyed by H2SO4 much easier, and some organics in the pristine BCS can be removed during the acid leaching (Rumpel et al., 2006). Cations can also be dissolved from the skeleton of aluminosilicate sheets, and relieve the hydration of exchangeable cations in clay minerals, thereby reducing the FSI. In contrast, the BCS treated by Na2CO3 (sample N-BCS) exhibits an extremely higher FSI (253%) than the P-BCS (120%).

For a given modification amount of APS, all the FSI decreased to the least value within 8 h. This indicates the reaction between pristine BCS and APS was almost complete after 8 h. For the addition of APS, i.e., 0.5Si (0.5 times of CEC), the FSI was practically constant at about 60%. For 2Si (2 times of CEC), the FSI decreased enormously and remained at about 50% after 4 h. Although the FSI was sometimes found to be unstable for 1Si (1.0 time of CEC), yet there was substantial decrement in FSI compared to the pristine BCS. For a given modification amount of APS, all the FSI decreased to the least value within 8 h. This indicates the reaction between pristine BCS and APS was almost complete after 8 h. It is necessary to introduce acid or alkaline to accelerate the reaction rate of APS modification.

The FSI plots of H-BCS (a) or N-BCS (b) samples which were modified by APS were displayed in Figure 4a and b, respectively. The initial point at zero time shows a lower FSI value (35%, see Figure 4) than those of P-BCS modified by APS (~120%, Figure 3), suggesting the importance of liquid-immersion. It is obvious the FSI was decreased after modification.
of APS. The FSI of H-BCS was found to decrease from 35% to 24% and further to 15% when the H-BCS was modified with 1.0Si and 2.0Si amount of APS (Figure 4a). Another finding is the faster reaction due to the Na2CO3 or H2SO4 treatment. The minimum value of FSI was found at about 8 h after the APS modification. When BCS was treated with H2SO4 followed by APS modification (Figure 4a) the FSI decrement was most pronounced. The minimum FSI was observed at 8% when 2.0 times CEC of APS was employed for soil modification. The reaction between APS and soil was also observed to be completed within 8 h. It was indicated that the structure of smectites was partly destroyed by H2SO4, and functional groups such as –OH, –SO3- were produced. These groups were active sites for immobilization of APS. Reactions between APS and soil can be considered as silane hydroxylation. The treatment with Na2CO3 followed by APS modification was found to have similar trend in the FSI, but the final FSI value (50%–60%) is much higher than H-Si-BCS samples (Figure 4b). This might be explained by the fact that although Na2CO3 helps the hydrogenation/immobilization of APS, yet this immobilization only occurs on OH− that was produced by hydration of Na2CO3 with aid of water. The hydrogenated APS was indicated to combine with free ions of OH− but not to clay particles, and thus the swelling ratio of particles (N-Si-BC) was not decreased too much. In a different style, H2SO4 was indicated to be more effective in diminishing the aluminosilicate structure of clay minerals in BCS, and the interaction between APS and clays becomes directly linked. Owning to the strong interaction and full coverage of APS, the amount of water up-taken by BCS will be less, and hence lower FSI values were achieved (Chen et al., 2010).

The effect of temperatures on the FSI during the APS modification was shown in Figure 5. All FSI values were found to decrease gradually with increasing temperatures. When the temperature reached 80 °C, the FSI values were minimized, and the decreased FSI values were found at this temperature, suggesting the modified silane by BCS is saturated. Compared to the FSI of pristine BCS and those modified samples (N-Si-BCS and H-Si-BCS), higher temperatures are key factors to achieve a lower FSI (60%–5%). The experiment indicated that the FSI of P-BCS can be decreased from 120% to 15% after treatment of H2SO4 and APS at the temperature up to 80 °C. Although the high temperature (~80 °C) could be difficult in practical engineering, this result could provide guidance for liquid (APS) treatment of swelling soils.

The UCS gives direct evidences for potential use in practical construction. Specimens (P-BCS, N-Si-BCS, H-Si-BCS) with different dosages of APS were prepared at the water content of 25% which as assumed to be the optimum moisture content (OMC) based on our previous finding (Miao et al., 2017). As can be found in Figure 6, the maximum UCS was found at the APS content of 1.0Si. Both the H-Si-BCS and N-Si-BCS were observed to have UCS higher than 0.7 MPa, which means the liquid immersed BCS with APS modification meets the criteria requirement by the road subgrade course (Patel and Shahu, 2015). Although the APS modified BCS (either treated with H2SO4 or Na2CO3) has less strength than those composite sample prepared by geopolymerization (Miao et al., 2017), this procedure by using liquid immersion would make this strategy feasible under some conditions.

3.2. Structural characterizations

To study the structural transformation as well as mechanism during the soil treatment, characterizations such as XRD, Fourier transform infrared spectrometric measurements (FTIR), scanning electron microscopic (SEM) observation, thermogravimetric (Shirini et al., 2013) analysis, and Zeta (ξ) potential measurements were conducted. As is shown by the XRD profiles in Figure 7a, the layered structure of smectite was found in P-BCS, but these layered structures were less observable after treatment of Na2CO3 or H2SO4. The right-shift of basal reflection in
the Na2CO3-treated BCS suggested the interlayer was collapsed to some extent. The large radius ions such as Ca2+ and Mg2+ could be replaced by Na+ after the Na2CO3 treatment, and the interlayer spacing is thus reduced (Rumpel et al., 2006). The basal reflection in the H2SO4-treated BCS exhibited a much broader manner, suggesting the lower crystallinity or the lamellar structures were partly destroyed. After APS was added into BCS as show in Figure 7b, the APS did not destroy layer structures of smectite, but there were slight differences in the interlayer spacing (d_{001}). For example, after APS modification the d_{001} was increased from 1.48 nm to 1.66 nm and further to 1.74 nm in case of H-BCS and N-BCS, respectively. It was indicated that some of the APS molecules were intercalated in the clay. Due to the longer length of APS, ca. 0.46 nm, the enlarged gallery indicated the APS adopted a bilayer model within interlayers of smectites (Shen et al., 2008). It was worth noting that the layered structure in H2SO4-treated BCS reappeared after APS modification. This implicated that APS re-constructed the lamellar structure after reacting with the –OH groups. It was known that the APS molecule shared a chain structure, and the functional groups at both ends provided different hydrophobicity. On condition that the hydrophilic group was combined with hydroxyl groups of the clay sheets, and the other hydrophobic end could be exposed to the outside. This type of sealing effects would prevent further hydration of the interlayered cations.

![Figure 6. APS dosage effects on the UCS of P-BCS and those treated with H2SO4 (H-Si-BCS) or Na2CO3 (N-Si-BCS).](image)

![Figure 7. (a) The XRD profiles of BCS treated with H2SO4 and Na2CO3 solutions; (b) The XRD patterns of H-BCS or N-BCS modified with APS.](image)

![Figure 8. The FTIR spectra of BCS and its modified soil samples.](image)

![Figure 9. (a) TG curves of pristine BCS and modified BCS with different means (b) TG curves of different content of modified BCS pre-treated with Na2CO3.](image)
Therefore the FSI of BCS was reduced or even diminished. In addition, the H₂SO₄ or Na₂CO₃-treaments of BCS would not have serious effects on the underground water if this method was applied in practical engineering because the filtrate (described in the experimental section) was almost neutral in view of pH values (~6.8 for H₂SO₄-treatment, ~8.4 for Na₂CO₃-treament). This suggested the complete consumption of acids in the BCS treatment.

The FTIR spectra of pristine BCS and the modified soils were illustrated in Figure 8. Bands of 1639 cm⁻¹ and 1401 cm⁻¹ corresponding to stretching vibrations of interlayer water, and the band 1035 cm⁻¹ indexed to Si–O–Si stretching vibrations were observed in all samples, indicating the structure of smectites were preserved in the modified BCS (Wu et al., 2014). Bands within 3000–3750 cm⁻¹ assigned to –OH (Si–OH, Al–OH and Mg–OH) stretching vibrations were also found in the pristine BCS, but the relative intensity (vs. Si–O–Si stretching vibration) became weakened after APS modification, suggesting the –OH groups were sealed with silane molecules (Su et al., 2013). These interactions have also been confirmed by Nuclear Magnetic Resonance (NMR) characterization (Caravajal et al., 1988). The modified BCS exhibited bands at 2923 cm⁻¹ and 2853 cm⁻¹ which can be indexed to stretching vibrations of –CH₂, and this indicates the APS was grafted on the BCS (Shen et al., 2007). By comparing the relative intensity of P-BCS modified with APS, the stretching vibration of –CH₂ was enhanced gradually after treatment with H₂SO₄ or Na₂CO₃, and the intensity was found to follow the order of silanes < Na₂CO₃ + silanes < H₂SO₄ + silanes, which suggested the H₂SO₄ treated BCS was more prone to react with APS.

The TG curves of pristine BCS and those modified BCS samples were displayed in Figure 9. The weight loss of free water and structural water were observed within the temperature region of 100–150 °C and 400–500 °C (Figure 9a). Compared to the pristine BCS, the percentage of free water was greatly reduced based on the weight loss within temperature of 100–150 °C. This could be attributed to the less amount of physically adsorbed water (Xi et al., 2004) when APS was modified. Due to the fact that dehydration reactions always occurred between silane (APS) and the –OH groups, the decomposition temperature and content

Figure 10. SEM images of BCS treated with different method (a) P-BCS, (b) Si-BCS, (c) Na-BCS (d) Na-Si-BCS, (e) H-BCS, and (f) H-Si-BCS

Figure 11. The Zeta potential of the BCS and those treated samples.
of adsorption water would be reduced after APS modification. According to curves in Figure 9b the modified BCS showed sharply weight loss at the temperature of 200–430 °C, suggesting the decomposition of silane at this temperature region. The mass percentage of APS calculated from the TG curve was roughly in accordance with the initial dosages of silane (see curves 0.5Si, 1.0Si and 2.0Si within 400–500 °C, Figure 9b), suggesting the complete reaction of APS.

Figure 10 displayed the SEM morphology of P-BCS and those treated samples. It was obvious that the P-BCS showed lamellar structures which are typical for clay minerals (Figure 10a). After the APS modification, irregular aggregates were observed (Figure 10b). When the BCS was treated with Na2CO3 the morphological transformation from P-BCS was not prominent (Figure 10c), but the APS modified Na2CO3-treated sample (N-Si-BCS) seemed to consist of more lamellae (Figure 10d). This can be explained by the fact that lamellar structures of smectites were re-constructed by APS as confirmed by the previous XRD analysis. In a different style the H2SO4 treated BCS (Figure 10e) and its corresponding APS modified sample (Figure 10f) showed less clay layers but more huge agglomerations instead. This morphological transformation suggested that the surface was greatly altered after APS modification, and the clay seemed to be aggregated as a result (Cui, 2009).

Zeta potential (ζ) is an important parameter to evaluate the stability of colloidal particles when they were dispersed in aqueous solution. The zeta potential of P-BCS was -40.5 mV. As shown in Figure 11, the APS modified BCS had zeta potentials of about -28 mV, which indicated the BCS aqueous dispersion was relatively stable. However, the H2SO4- or Na2CO3-treated BCS plus APS modification shared a lower zeta potential -14 mV, and these potentials afforded clay particles less stable in water. The sample of H2SO4-treated soil after APS modification showed the least zeta potential (-3.5 mV), and this sample is difficult to re-dispersed in water solution, i.e., there was no possibility to get hydronium ions when this sample was exposed to water. Based on the FTIR analyses, the hydrophilic group in APS reacted with the –OH of the clay soil, and the hydrophobic group was exposed to achieve surface hydrophobicity. The hydration of Si–O tetrahedron would not take place after this modification (Cui, 2009). The APS protection layer would avoid the entrance of water molecules, and therefore the FSI was almost diminished.

4. Conclusion

In conclusion, a liquid-treatment method of suppressing the swelling of BCS was developed, and the H2SO4 treatment was found to be most effective in getting a fast modification of BCS by APS. When BCS was treated with 7.5% H2SO4 and APS, the FSI of BCS was able to be decreased from 120% to 15%. Although the procedure reported in this research were still to be developed to meet the practical cost-effect because of the high price of APS, the deceased FSI value was readily acceptable in view of a basic science study (GB50112-2013). According to the XRD analysis, the (001) diffraction peaks of the modified BCS were left-shifted, indicating some silane molecules entered the smectite layer. The intensity of –OH peaks were greatly decreased or even disappeared in FTIR in the modified BCS, suggesting the silane was grafted on the BCS surface. As confirmed by the zeta potential measurements, the hydrophilic group of silane was demonstrated to react with –OH function groups of the inter-lamellar. After this reaction the hydrophobic group was exposed to the external surfaces, which makes the clay soil more hydrophobic. The hydration of cations was avoided, and the swelling was almost diminished.

Declarations

Author contribution statement

Shiding Miao: Conceived and designed the experiments; Performed the experiments.
Jinqiu Huang: Performed the experiments.
Peng Zhang, Wanglin Wen: Analyzed and interpreted the data.
Wenqing Li, Shaonan Xu: Contributed reagents, materials, analysis tools or data.
Weikun Ning: Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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