

Stabilisation of peat with colloidal nanosilica

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SUMMARY

Colloidal nanosilica hydrosols are electrochemically stabilised polymerised amorphous silica in low viscosity suspensions. They have no known adverse impact on soil health and ecosystem service functions, thereby having a scope for use in groundworks as an alternative low-viscose stabilising material. Six grades of colloidal nanosilica are synthesised through an in-house procedure and introduced to a natural peat soil. The peak and residual compressive strength of compacted and modified soils are measured immediately after treatment and in four strain levels post treatment. Findings suggest that, despite the direct correlation between the nanosilica content and compressive strength, an increase in nanosilica content does not necessarily offer stability at larger strains. This is a major limitation. The particle-level kinematics in modified peat is discussed to gain a new insight into the role played by silica flocs on the build-up of macro-mechanical quantities such as peak and critical state strength. Overall, modification of peat with nanosilica leads to improvements in strength and formation of composites with generally more dilative behaviour. When used as a single stabiliser, a design 15 % to 20 % grade nanosilica solution yields a reasonably high strength although precautions against excessive straining of modified peat soils need to be taken in the first seven days post treatment. At this optimum grade, the loss of strength on further straining is capped to 9 % at plastic strains 1.5 times the peak strain.

KEY WORDS: grout, hydrosol, organic, soil improvement, stiffness, strength

INTRODUCTION

Soils with an organic content above 20 % are universally known as organic soils. The term ‘peat’ is generally used for soils with organic content above 75 % (ASTM D4427). Bragg & Lindsay (2003) defined peat as “partly decomposed plant material that has accumulated in situ - rather than being deposited as a sediment - as a result of waterlogging”. Peat covers some 3 % of earth’s land area, occurring mainly in temperate and tropical climates and in the form of patchily distributed layers in peatlands (also known as bogs or mires). The organic matter is supplied by leaves, stems, root tissues and decomposed microorganisms that are slowly degraded over tens to thousands of years below the water table in swamps or wetlands (Jarrett 1997, Warburton *et al.* 2004, Youventharan *et al.* 2007, Xintu 2008, Kalantari 2013). This slow degradation results in carbon storage and sequestration. In the UK, the total weight of carbon locked in soil is estimated at 6.9 billion tonnes in Scotland, 2.8 billion tonnes in England and Wales (Ostle *et al.* 2009) and

0.4 billion tonnes in Northern Ireland (Cruickshank *et al.* 1998). Over 40 % of the carbon stored in soil is locked in peat. Globally, carbon stored in peat amounts to 600 Gt (Yu 2011), highlighting the significance of organic soils and peat in the context of climate change. Peat stores carbon as long as it remains wet. From an engineering perspective, peat is porous, soft, highly compressible, highly plastic and unconsolidated, with low shear strength (Barden & Berry 1965, Tremblay *et al.* 2002, Hebib & Farrell 2003, Kolay & Rahman 2016). At micro-scale, peat has a pH-dependent structure. When pH falls to neutral levels, peat gains an aggregated structure. At lower pH levels, peat adopts a slightly fibrous structure (Šķēls *et al.* 2013). Dewatering and drainage of peat ahead of construction leads to groundwater level drawdown and exposure of the peat to air, creating a thick oxic peat layer within which, upon raising pH, aerobic decomposition is favoured resulting in efflux of carbon as CO₂ into the atmosphere and promotion of the greenhouse effect. This brings two major problems. From an environmental point of view, the organic matter in



peat is a source of nutrients for flora and fauna and also functions as a permanent geological carbon sink. Release of carbon into the atmosphere as a result of human activities jeopardises the role of wetlands and organic matter in controlling global carbon emissions. From an engineering standpoint, drainage of peat leads to aerobic decomposition, cracking, subsidence and geomechanical complications (Jauhiainen *et al.* 2008, Sloan *et al.* 2018, 2019) which can, in part, be mitigated through piling (Satibi 2009), chemical stabilisation and grouting (Holm *et al.* 1983, Gulin & Wikström 1997, Axelsson *et al.* 2002), deep mixing with recycled fibrous and filling materials (Saberian & Rahgozar 2016) or opencast mining and replacement of peat with better quality soil (MacFarlane 1969). However, these engineering interventions lead to further decomposition of peat, disruption of its biogeochemical cycles, and degradation of its natural functions as a key component of healthy ecosystems.

Conventional mitigation techniques

A broad suite of commonly practised modification methods for peat and organic soils is reviewed by Edil (2003), including excavation and replacement, reinforcement, preloading, piling, thermal processing and stabilisation with cement and lime. Kolay & Pui (2010) reported an increase in the Unconfined Compressive Strength (UCS) of peat from 6.5 kPa to 44.9 kPa upon adding 6 % by mass of gypsum. For peat of almost similar initial strength, Wang & Leung (2008) demonstrated a by-and-large greater post-modification UCS of 179 kPa upon adding sand-cement mixture at 75:225 kg.m⁻³ (75:25 ratio in mass per cent). The effectiveness of sand-cement grouts is in agreement with the more recent findings of Nikookar *et al.* (2012), who reported an increase in UCS from an initial 45 kPa to 264 kPa on addition of 10 % by mass of cement and 10 % by mass of sand. For a peat of similarly low strength (UCS = 45 kPa), Said & Taib (2009) reported an increase in UCS to 115.5 kPa following addition of 12 % by mass of lime, lending further evidence of the relatively greater efficiency of sand-cement mixtures in peat stabilisation. Šķēls *et al.* (2013) mixed samples of very weak (UCS of about 18 kPa) fibrous peat obtained from Riga with Portland cement (200–300 kg of cement per cubic metre), applied a range of surcharge pressures (up to 18 kPa) to the fully saturated mixtures and retained the pressures for 7, 14 and 28 days. In the absence of surcharge and for the relatively low 200 kg cement per cubic metre of soil-cement mixture, they showed an increase in UCS to 113 kPa after 28 days. This is almost equal to the UCS reached by Said & Taib (2009) on addition of

12 % lime, indicating limited improvement. The maximum post-modification strength reached was 350 kPa after 28 days under 18 kPa surcharge and for the relatively high 300 kg cement per cubic metre of soil-cement mixture. They concluded that surcharge plays a key role at early stabilisation stages. In later stages, the cement content takes pronounced control of the stabilisation process. The ASTM D4609 standard places the UCS value in context and offers insight into the effectiveness of different chemical stabilisation methods. According to ASTM D4609, and for stabilisation to be deemed effective, the UCS in modified soil needs to be above 345 kPa.

Limitations

The uncertainty associated with the effectiveness of chemical additives in stabilisation of peat suggests that the organic content of peat is likely to interfere with the stabilisation process to some degree. The interference is likely to be in the form of interactions among organic substances, soil minerals and additives, as organic matter coats mineral particles and impedes the hydration (Åhnberg *et al.* 1995, Tremblay *et al.* 2001). Interference can also take the form of disruptions in pozzolanic reactions, with implications for the properties of C-S-H binders. This is a major drawback to using calcium-based pozzolans for the improvement of peat.

Organic matter is essentially non-humic remnants of micro-organisms that, with time, transform into polysaccharides and carbohydrates, and then weather into humic substances. Assadi Langroudi *et al.* (2019) recently looked into the effects of polysaccharides on hydromechanical properties (pore anatomy, structure, and structure-based stress-strain behaviour) of clayey silts. Using Fourier Transform Infrared Spectroscopy, they traced the interference of methoxyl pectin (a complex set of polysaccharides and albumen) in pozzolanic reactions. They specifically addressed pozzolanic reactions between clay, bicarbonates, H-silicates and calcium.

Sodium bicarbonates in loamy soils typically originate from weathering of alumina-silicate minerals through carbonation. H-silicates and amorphous silica precipitates originate from hydration of Na-minerals that are naturally abundant in the soil's clay fraction. Assadi Langroudi *et al.* (2019) used IR bands associated with Ca-OH and Si-O stretching vibrations and showed a strong decrease in intra-lattice pore volumes, as well as a substantial increase in air entry value, plasticity and shrinkage limit upon the formation of complex chains of deprotonated clay - pectin - cation - pectin. They also used major mid-IR bands for C-S-H gels associated with Si-O and Si-O-Si stretching

vibrations and showed interference by organic matter with pozzolanic reactions through depolymerisation of the silicate chain and effects on the composition of C-S-H gels.

Scope for use of alternative more sustainable additives

Colloidal nanosilica (NS) hydrosols are electrochemically stabilised polymerised amorphous silica in low viscosity suspensions; they are also available in the form of hydrated gels, silica globules or pellicles. There have been some previous attempts to use silica-based binders to stabilise loose sands (Kaga & Yonekura 1991, Kodaka *et al.* 2005, Porcino *et al.* 2012) and loess (Haeri *et al.* 2015) which demonstrated scope for removing collapsibility and liquefaction potential, and for enhancing peak shear strength. Haeri *et al.* (2015) mixed a parent loess soil with nanosilica hydrosol, adjusted the water content to a constant 15 %, and applied a standard Proctor compaction energy. The open structure of the loess was disturbed and, for this reason, the reported increase in strength is possibly due to the coating effect of nanosilica particles. Pham & Nguyen (2014) presented experimental findings to show scope for relaxation of swelling properties of clays through treatment with NS solution. Despite the uncertainties associated with possible chemical interactions between colloidal NS and soil minerals, as well as possible effects of the resulting binary structures on post-peak stress-strain behaviour and particularly static flow potential, silica-based hydrosols do not have any known adverse impact on soil health and ecosystem service functions and this makes them attractive as a potential alternative low-viscose grout for peat modification.

This contribution presents experimental evidence on the use of NS grout in the stabilisation of peat. A total of six colloidal NS solutions are added to a base peat soil, and the mixtures are compacted at optimum water content and cured under controlled ambient conditions for four different curing periods. Twenty-five unconfined compressive strength (UCS) tests are conducted, each repeated three times to accommodate the exceptionally high spatial variability in the properties of organic soils. The UCS test alongside the California Bearing Ratio (CBR) test are universally popular and widely used in the design of earthworks. Due to the limitations of the UCS test for evaluating the stress-strain behaviour of soils and particularly the post-peak response, the findings from the UCS tests are used here merely as an index to compare treated and untreated peat samples.

METHODS

Urmia Lake peat

The material tested in this study is a natural highly organic soil containing <50 % organic matter obtained from the Urmia–Tabriz Shahid Kalantary Highway, 8 km east of Urmia City, Iran (Figure 1). This region is nationally recognised for its challenging ground conditions. The peat soil is capped with 40 cm of alluvium and extends to about 12 m depth, meaning it is classified as ‘deep peat’ according to Andriess (1988). The terms ‘peat’ and ‘peat soil’ are used interchangeably to refer to the testing material. A stainless steel double blade cutter (Wardenaar type peat corer) with sharpened edges was used to retrieve one 10 × 10 × 100 cm core sample from the bottom of each of five 1.5 m deep open trenches excavated at 6 m intervals in the late spring of 2018, when the peat was moderately wet. Coring was conducted in stages. The first blade of the corer was pushed vertically into the peat, cutting round part of the core’s perimeter. The second blade was then inserted vertically to cut the remaining sides of the core. Finally, both blades were extracted together with the encapsulated core. The undisturbed samples thus retrieved were used in a wider research programme, with only a fraction of the material being used in the present study. The extracted peat was dark brown in colour and spongy in nature (Figure 1). The peat samples from all boreholes were mixed to create a uniform single sample for testing.

The extracted material was classified according to degree of decomposition/humification on the von Post scale (von Post 1922). There are ten degrees of decomposition in the von Post scale, ranging from H1 (fibrous and undecomposed) to H10 (amorphous and decomposed). The peat samples obtained can be confidently classified as H5. This is in good agreement with earlier assessments of soil in the study site (Badv & Sayadian 2011, 2012).

BS1377 and ASTM D2216 set out the standard method for determination of (gravimetric) soil water content through oven-drying. The mass of moist soil is conventionally reduced by oven drying at a temperature of 110 ± 5 °C. The equilibrium oven dried mass is typically reached between 12 and 24 hours and after recording three consecutive equal masses. This method assumes that the reduction in mass is entirely due to the evaporation of pore water. For organic soils, however, drying at 110 ± 5 °C can cause loss of mass from the solid phase due to charring of the organic fraction. Loss of organic mass from the solid phase may begin at 80–85 °C (MacFarlane & Allen 1965) and, to avoid this, Jarrett

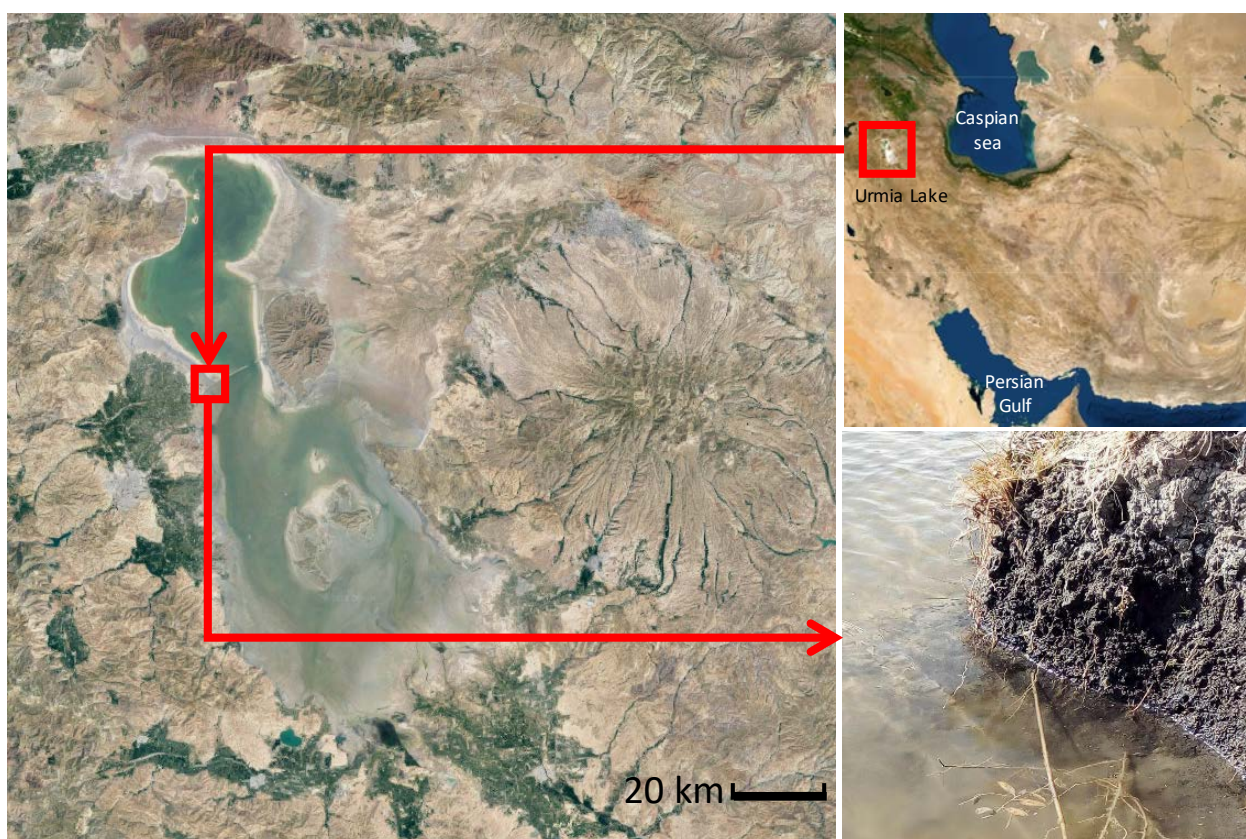


Figure 1. Left and top right: aerial images showing the location of the study site on the Urmia–Tabriz Shahid Kalantary Highway, 8 Km east of Urmia, Iran. Bottom right: the appearance of the sampled peat layer.

(1983) suggested drying at 60–80 °C. For peat, ASTM D2216 (1998) suggests a 60 °C drying temperature. In this study, natural water content was determined by drying the peat samples in an oven for 48 hours at 50 °C to avoid charring, meaning that small quantities of pore water which would evaporate at 110 ± 5 °C remained in the test specimens.

The standard Casagrande method was used to determine the consistency limits. X-ray Fluorescence (XRF) spectroscopy was used for elemental analysis of the natural peat soil. The organic content (OC) was obtained by burning the soil at 600 °C in a furnace and determining the Loss on Ignition (LOI). Samples were regularly weighed and retained in the furnace until no further changes in measured mass were recorded. The Loss on Ignition was then calculated in compliance with the ASTM 2974 standard method. pH measurement was performed in compliance with the ASTM D4972-95a (Method A) test method, using a Hanna bench-top pH meter. Table 1 summarises the physical properties of Urmia peat.

Nanosilica hydrosol

Commercial colloidal nanosilica (NS) was supplied in kind by ISATIS Silica Group (Yazd, Iran) and used to prepare six NS suspension grades. The material is

mostly used as additive in cement mortars and is commonly added to cement using the modified Stöber method for synthesis of nanosilica particles, which involves the simultaneous application of nanosilica - tetraethyl orthosilicate, ammonia catalyst and ethanol in water (Sikora *et al.* 2015). The material was supplied in the form of 30 % (by weight) NS solution (hydrosol) with a low viscosity of 5.5 cP (1 cP = 1 mPa·s), a pH of 10, a density similar to water (1.1 g cm^{-3} at 20 °C) and an average particle size of 16 nm. Tables 2 and 3 summarise the physical and chemical properties of the hydrosol. Distilled water was added to the hydrosol to form graded NS suspensions (5 %, 10 %, 15 %, 20 %, 25 % and 30 % by weight). The pH of the suspensions was then lowered to 6 by mixing them with sodium chloride (NaCl) electrolyte and an aqueous solution of hydrochloric acid (HCl). This led to collision of solid matter, formation of siloxane bonds and rapid polymerisation. The gel time (i.e. the time required for the viscosity to increase above 1 cP) was found to be about 570 ± 20 minutes through trial and error, which is generally consistent with previous attempts (Agapoulaki & Papadimitriou 2015). The silica solutions were finally given 24 hours of curing time to set.

Table 1. Physical and chemical properties of Urmia Lake peat.

| | |
|---|---------|
| Depth of sampling (m) | 1.5 |
| Natural water content (w) (%) | 45 |
| Degree of decomposition | H5 |
| Organic content (%) | 49.6 |
| Calcium carbonate CaCO ₃ | Trace |
| Void ratio (e) | 3.89 |
| Moisture of saturation (w) (%) | 102–671 |
| Bulk density (γ) (kN.m ⁻³) | 9.59 |
| Liquid limit (%) | 153 |
| Plastic limit (%) | 82 |
| Plasticity index (%) | 71 |
| pH | 8.1 |
| Specific gravity (G _s) | 1.84 |
| Optimum water content (%) | 29 |
| Maximum dry density ($\gamma_{d\ max}$) (kN.m ⁻³) | 12.25 |
| SiO ₂ (%) | 46.82 |
| Fe ₂ O ₃ (%) | 6.08 |
| Al ₂ O ₃ (%) | 12.44 |
| Na ₂ O (%) | 0.53 |
| CaO (%) | 8.69 |
| MgO (%) | 2.78 |
| SO ₃ (%) | 0.77 |
| K ₂ O (%) | 2.27 |

Table 2. Physical properties of nano-SiO₂.

| | |
|---|---------|
| Purity (%) | 99 |
| Average particle size (nm) | 16 |
| Specific surface area (m ² g ⁻¹) | 600–785 |
| Bulk density (g cm ⁻³) | 0.1 |
| Real density (g cm ⁻³) | 2.4 |
| Colour | White |

The significance of hydrosol pH is well established. Sikora *et al.* (2015) recently reported enhanced intensity of X-Ray Diffraction microgram at $2\theta = 29.2^\circ$ following 7 days of hydration of nanosilica-cement composite mortar, suggesting enhanced levels of pozzolanic reactions. The elevated levels of hydration correlated directly with the diameter of the nanosilica spheres, which itself is a function of the pH and temperature of the hydrosol.

Specimen preparation and mechanical procedures

Natural peat from the study site was transferred to the laboratory and stored at ambient temperature ($20 \pm 3^\circ\text{C}$). The standard Proctor compaction test (ASTM D698-12e2) was conducted on wet peat soil and repeated three times to accommodate the strong variability of data arising from the high organic content of peat soil. The peat soil was passed through a 0.42 mm sieve before compaction. The dry unit weight is plotted against compaction water content in Figure 2, indicating an optimum water content of 29 % and a maximum dry unit weight of 12.0 kN m^{-3} , and highlighting the high water retention capacity and low solid density of peat.

Two series of natural and stabilised peat specimens were synthesised using standard Proctor compaction at optimum water content. The peat was initially dried at 50°C for 48 hours, then thoroughly mixed with deionised water to raise its moisture content to the 29 % optimum (Table 1). The wet material was then allowed to rest for 24 hours in sealed plastic bags, to ensure that the water distributed

Table 3. XRF elemental analysis for nano-SiO₂.

| Element | % |
|--------------------------------|-------|
| SiO ₂ | 33.96 |
| Fe ₂ O ₃ | 0.07 |
| Al ₂ O ₃ | 0.27 |
| Na ₂ O | 5.017 |
| CaO | 0.07 |
| MgO | 0.046 |
| SO ₃ | 0.097 |
| K ₂ O | 0.12 |
| Cl | 0.35 |
| P ₂ O ₅ | 0.11 |

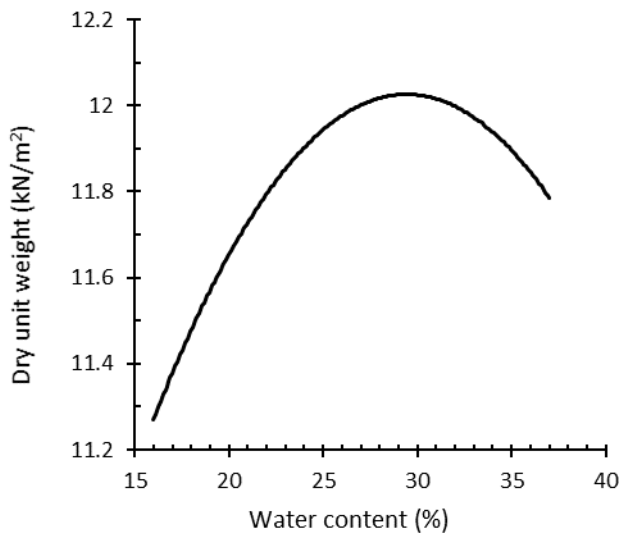


Figure 2 Standard Proctor compaction curve for extracted peat soil:

$$w_{opt} = 29\%; \quad \gamma_{d-max} = 12.01 \text{ kN m}^{-3}.$$

uniformly throughout the pore spaces. For chemically modified specimens, the adjusted NS solutions (i.e. 5–30 % suspensions) were added to the wet peat and mixed thoroughly using a standard mechanical mixer. The mixtures are summarised in Table 4. The soil was compacted in 101.4 mm compaction moulds in three layers, employing the standard Proctor compaction energy. Cylindrical test specimens, 38 mm in diameter and 80 mm high, were then extracted by pushing sharpened stainless steel sampling tubes into the block of compacted soil using a hydraulic jack. Extracted specimens were wrapped in thin plastic film and stored in an environmental chamber at 20 ± 3 °C ahead of mechanical testing on the 1st, 7th, 14th and 28th days.

Series of strain-controlled Unconfined Compressive Strength (UCS) tests were carried out on the compacted specimens in compliance with the ASTM D2166 / D2166M-16 standard. To address the high variability of UCS values from unconfined loading of soils, each loading experiment was repeated twice on identical specimens to determine the average UCS value for each testing point. Specimens were loaded at a rate of 1 mm min^{-1} in a standard compression testing load frame. This rate was deemed suitable for minimising creep deformations. Peak and post-peak response was captured in the form of stress-strain curves.

Scanning Electron Microscopy (SEM) was used to study the particle-level kinematics. Vertically aligned cubic soil samples (5–7 mm) with one undisturbed fractured face were cut and viewed under a Philips XL-30 LaB6 (general purpose $50 \times 50 \text{ mm}$

Table 4. Mixture composition.

| Specimen | Unit weight (kg m^{-3}) | | |
|----------|------------------------------------|-------|-------|
| | peat | water | NS |
| S(0) | 1201.0 | 348.0 | 0.0 |
| S(5) | 1141.0 | 348.0 | 60.0 |
| S(10) | 1080.9 | 348.0 | 120.1 |
| S(15) | 1020.9 | 348.0 | 180.1 |
| S(20) | 960.8 | 348.0 | 240.2 |
| S(25) | 900.8 | 348.0 | 300.2 |
| S(30) | 840.7 | 348.0 | 360.3 |

stage) microscope. To obtain these samples, tested specimens were air-dried under ambient indoor conditions (23 ± 2 °C) over the course of 3–4 weeks, broken by hand into two half-cylinders and then into sectors, and finally trimmed on five sides using a surgical knife (scalpel). The samples were then installed on aluminium SEM stubs using hardener and resin. Loose particles were removed from the fractured face by turning the stub upside-down several times. The samples were vacuumed to 0.15 Torr and vacuum-coated with carbon before imaging.

RESULTS

In the first column of Table 5, the nanosilica (NS) content is indicated in brackets, followed by the curing period in days; for example, S(15):14 stands for peat mixed with 15 % by weight of NS solution and cured for 14 days. The next four columns of Table 5 show the secant elasticity modulus (E), UCS, peak unconfined strength (q_p) and axial strain at peak (ϵ_p). The retained compressive strength on further post-peak straining is used here as a proxy for degree of brittleness of the test specimens; specimens were loaded to their peak strength, then further strained to $\epsilon_{ri} = i \cdot \epsilon_p$, where i varies from 1.5 to 2.5 in intervals of 0.5. The retained compressive strength is defined here as the quotient of compressive strength at ϵ_{ri} and compressive strength at peak, represented in Table 5 by \bar{q}_j , where $\bar{q}_j = q_{\epsilon_{ri}}/q_p$. In this, \bar{q}_j represents the proportion of the peak compressive strength retained at plastic strains, with $\bar{q}_j = 1$ representing no loss of strength from peak and $\bar{q}_j = 0$ representing total loss of strength from peak.

A strongly ductile behaviour appeared in compacted base peat soil. The maximum

compressive strength was recorded at a low 23.2 kPa and at 15.2 % axial strain, after which stress remained constant with further straining.

The compressive strength increased by 40 % immediately after introduction of the 5 % NS solution. A 326 % increase was recorded upon addition of the 30 % NS solution, inferring a direct correlation between NS content and compressive strength (up to 30 % added NS). Long after treatment, this direct correlation remained. Immediately after treatment, strain at peak decreased to a low 2.5 % to

3.1 %, demonstrating the much more brittle behaviour of modified peat samples. The \bar{q}_j decreased with increasing NS content to a low of 0.5 in S(25):1, before rising again for NS content greater than 25 %. Similar trends were observed in stabilised samples cured for 14 days: the peat samples stabilised within two weeks after treatment, with 25 % NS solution yielding the lowest residual strength as strains grew to 1.5 % plastic strain. Our observations here led to the key finding that residual strength appears to be inversely proportional to NS content for

Table 5. Testing diet and results. E = secant elasticity modulus, UCS = Unconfined Compressive Strength, q_p = peak unconfined strength, and ϵ_p = axial strain at peak. The remaining columns show retained compressive strength on post-peak straining; see text for further explanation.

| Specimens | E (kPa) | UCS (kPa) | q_p (kPa) | ϵ_p | \bar{q}_1 (kPa) | | | \bar{q}_2 (kPa) | | | \bar{q}_3 (kPa) | | |
|-----------|--------------|--------------|----------------|--------------|-------------------|---------------------|-------------|-------------------|---------------------|-------------|-------------------|---------------------|-------------|
| | | | | | ϵ_{ri} | $q_{\epsilon_{ri}}$ | \bar{q}_j | ϵ_{ri} | $q_{\epsilon_{ri}}$ | \bar{q}_j | ϵ_{ri} | $q_{\epsilon_{ri}}$ | \bar{q}_j |
| S(0) | 147.2 | 23.07 | 23.2 | 0.152 | - | - | - | - | - | - | - | - | - |
| S(5):1 | 1613.5 | 31.66 | 32.6 | 0.031 | 0.046 | 28.49 | 0.87 | 0.062 | - | - | 0.077 | - | - |
| S(5):7 | 1899.7 | 55.84 | 53.1 | 0.028 | 0.042 | 54.26 | 1.02 | 0.056 | 51.57 | 0.97 | 0.070 | 41.33 | 0.78 |
| S(5):14 | 2379.3 | 73.67 | 73.8 | 0.030 | 0.045 | 69.04 | 0.93 | 0.060 | 36.96 | 0.50 | 0.075 | 20.57 | 0.28 |
| S(5):28 | 3456.2 | 109.98 | 109.7 | 0.028 | 0.042 | 102.1 | 0.93 | 0.056 | 87.46 | 0.80 | 0.070 | 73.13 | 0.67 |
| S(10):1 | 2182.7 | 56.21 | 56.7 | 0.027 | 0.040 | 49.37 | 0.87 | 0.054 | 29.53 | 0.52 | 0.067 | 20.06 | 0.35 |
| S(10):7 | 2360.7 | 65.86 | 63.0 | 0.026 | 0.039 | 59.30 | 0.94 | 0.052 | 63.80 | 1.01 | 0.065 | 55.79 | 0.88 |
| S(10):14 | 4498.7 | 103.47 | 102.6 | 0.025 | 0.038 | 85.41 | 0.83 | 0.050 | 54.15 | 0.53 | 0.062 | 23.30 | 0.23 |
| S(10):28 | 3572.4 | 132.01 | 132.2 | 0.032 | 0.048 | 74.80 | 0.56 | 0.064 | 26.79 | 0.20 | 0.080 | 10.80 | 0.08 |
| S(15):1 | 2071.6 | 65.89 | 65.8 | 0.031 | 0.046 | 38.68 | 0.59 | 0.062 | 36.02 | 0.55 | 0.077 | - | - |
| S(15):7 | 3652.0 | 95.23 | 94.2 | 0.023 | 0.034 | 72.29 | 0.77 | 0.046 | 50.80 | 0.54 | 0.057 | 31.11 | 0.33 |
| S(15):14 | 4409.8 | 108.53 | 108.4 | 0.024 | 0.036 | 72.85 | 0.67 | 0.048 | 52.63 | 0.48 | 0.060 | 27.41 | 0.25 |
| S(15):28 | 4960.8 | 162.59 | 162.4 | 0.029 | 0.043 | 105.60 | 0.65 | 0.058 | 28.69 | 0.18 | 0.072 | - | - |
| S(20):1 | 2720.4 | 67.60 | 67.9 | 0.026 | 0.039 | 35.77 | 0.53 | 0.052 | 16.76 | 0.25 | 0.065 | 5.00 | 0.07 |
| S(20):7 | 3677.1 | 103.32 | 103.2 | 0.027 | 0.040 | 70.14 | 0.68 | 0.054 | 41.55 | 0.40 | 0.067 | 11.31 | 0.11 |
| S(20):14 | 4672.8 | 141.57 | 139.6 | 0.026 | 0.039 | 72.63 | 0.52 | 0.052 | 21.31 | 0.15 | 0.065 | - | - |
| S(20):28 | 7374.8 | 175.52 | 175.5 | 0.024 | 0.036 | 159.60 | 0.91 | 0.048 | 48.21 | 0.27 | 0.060 | 10.28 | |
| S(25):1 | 2977.5 | 81.85 | 83.5 | 0.025 | 0.038 | 42.17 | 0.50 | 0.050 | 13.89 | 0.17 | 0.062 | 2.50 | 0.03 |
| S(25):7 | 4886.3 | 130.85 | 131.8 | 0.026 | 0.039 | 70.14 | 0.53 | 0.052 | 29.61 | 0.22 | 0.065 | 4.50 | 0.03 |
| S(25):14 | 7599.0 | 159.96 | 162.2 | 0.021 | 0.031 | 129.10 | 0.79 | 0.042 | 38.84 | 0.24 | 0.052 | 14.45 | 0.09 |
| S(25):28 | 9355.5 | 251.06 | 251.0 | 0.028 | 0.042 | 140.90 | 0.56 | 0.056 | - | - | 0.070 | - | - |
| S(30):1 | 4155.4 | 98.26 | 98.9 | 0.025 | 0.038 | 67.07 | 0.68 | 0.050 | 46.90 | 0.47 | 0.062 | 33.30 | 0.34 |
| S(30):7 | 6000.0 | 149.95 | 150.5 | 0.025 | 0.038 | 133.01 | 0.88 | 0.050 | 61.43 | 0.41 | 0.062 | 28.03 | 0.19 |
| S(30):14 | 7222.8 | 180.57 | 180.0 | 0.028 | 0.042 | 104.00 | 0.58 | 0.056 | 26.32 | 0.15 | 0.070 | 3.30 | 0.02 |
| S(30):28 | 9782.7 | 283.74 | 184.2 | 0.029 | 0.043 | 66.73 | 0.36 | 0.058 | 16.71 | 0.09 | 0.072 | 2.00 | 0.01 |

5–25 % NS solutions. Curing time appears to play a pivotal role. Peat samples stabilised with 20 % NS solution offered maximum residual strength 28 days post treatment. In other words, despite the direct correlation between NS content and compressive strength discussed earlier, an increase in NS content does not necessarily offer stability at large strains. This is a major limitation which is studied further here using micro-scale techniques.

In Figure 3a, the $q - \varepsilon$ (stress-strain) curve for modified peat with $\leq 20\%$ NS hydrosol exhibits some clearly visible jigsaw fluctuations that represent periods of rapid interaction between base peat soil particles and NS floc units, suggesting rapid rearrangement of particles and thus a turmoil in both fabric and interparticle forces. The electron microscopy images in Figure 4 show an aggregated NS floc in between silt-sized quartz particles and organic matter fragments of various sizes. The

rounded shapes of the flocs infer a history of polymerisation of silica into the form of coagulated units or flocs (globules) in the soil solution before the flocs precipitate to form ‘trapdoors’ in the necks of soil pores. Hence, the flocs sit in between the base soil particles and play a fundamental role in the appearance of sawtooth fluctuations. Figure 3a suggests that fluctuations persist until the particles attain a more stable packing state, and that volatilities are less pronounced at higher NS contents; a change of state that is consistent with the diminishing loss of strength (upon post-peak straining) with increasing NS content. The greater degrees of fluctuation seen at lower NS content can be attributed to the links between NS load (in colloidal solution), elapsed precipitation and setting time, precipitation rate and micro-morphology. As the NS nuclei grow with increasing precipitation time and silica content, upturned amorphous silica plates collide to form

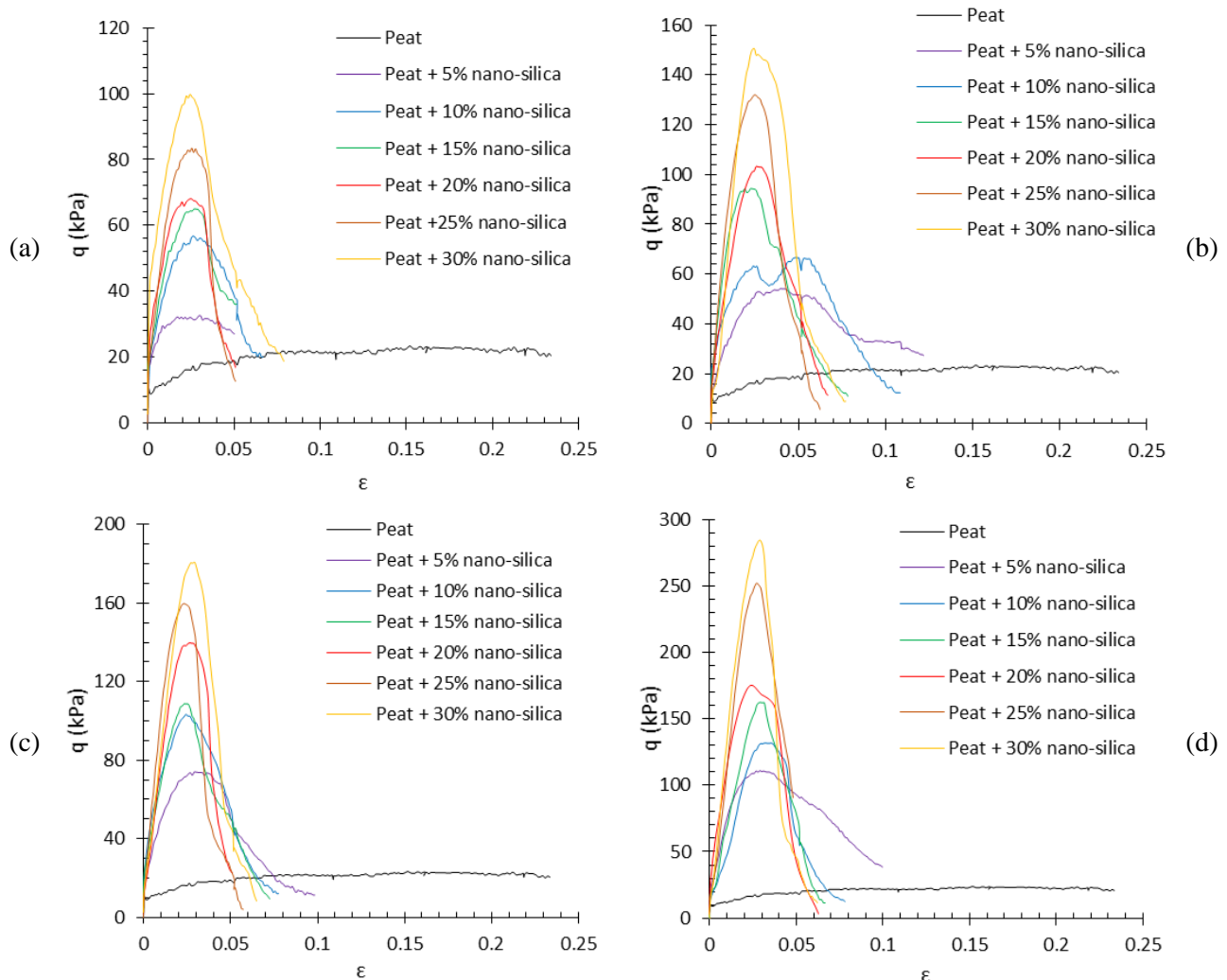


Figure 3. Stress-strain response of optimum compacted natural peat and modified peats with nano-silica colloidal solutions, with curing times (a) 1 day, (b) 7 days, (c) 14 days, (d) 28 days.

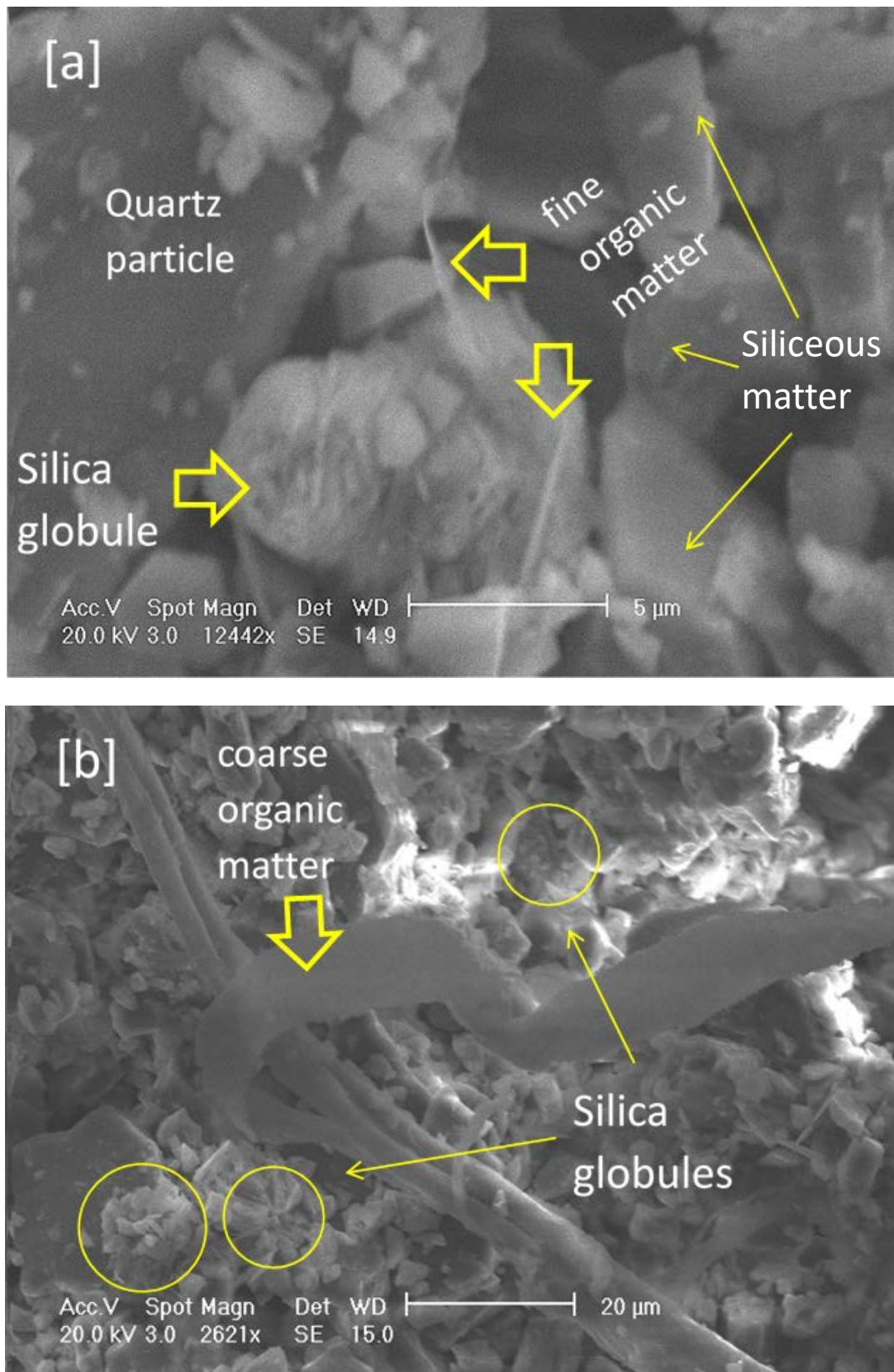


Figure 4. Two SEM micrographs of modified peat specimens: [a] basic elemental level at 12000 \times magnification, showing the perturbed plates within the rounded silica globules surrounded by a suite of organic and siliceous solid matter; [b] domain level at 2000 \times magnification, showing the morphology of fibrous organic matter and larger silica coagulates in between domains of siliceous solid matter and macropore spaces.

rounded globules which gain diameter and strength with setting time. The more pronounced fluctuations at lower silica content are associated with a more platy texture of the silica globules.

Fluctuations ceased in Specimen S(10):1 when the geo-composite soil was axially stressed at strain levels above 3.2 % (i.e. 0.032 in Figure 3a). Here, the $q - \varepsilon$ curve trends to a plateau before dipping, marking a steady state in which the specimen achieves a local minimum strength ahead of strain-softening. This transition marks the most pronounced loss of particle-to-particle contacts. The subsequent strain-softening period leads to a decrease in the mean particle-to-particle contact number and is generally referred to as 'flow'. The possible micro-mechanisms behind fluctuations are speculative but interesting. As strain increases, the rounded NS flocs in the granular assembly naturally tend to roll on the base soil particles to reach a locally stable state. At this steady state, the flocs supply maximum confining pressure to the array of particles, allowing them to achieve a critical maximum sum of normal contact forces that coincides with a peak value in the tangent contact forces. When the array moves from maximum strength towards onset of flow, the flocs roll into macro-pore space, the lateral confinement disappears, and the soil system consequently enters a phase of strain softening.

Figure 3b shows the $q - \varepsilon$ variation in modified specimens after seven days of curing time. For modified soils with up to 15 % NS content, the diagram presents a clear double peak stress-strain response. It is assumed here that a longer curing period leads to formation of relatively stronger flocs of larger diameter. At the peak strain, flocs move towards the macro-pore space but, owing to their large diameter, form what appears to be a suite of inter-particle trapdoors. The trapdoors compensate for the lost lateral confinement, leading to a short spell of strain-hardening towards a second peak, at which point the flocs roll into the macro-pore space.

By and large, the double peak becomes more pronounced at 10 % NS content (i.e. S(10):7) and in all cases it is followed by a period of strain-hardening before the soil reaches the critical (or steady) state. At the critical state, the volume of the soil system - under increasing load - does not change in time. The critical state on the $q - \varepsilon$ curves disappears as NS content increases beyond 20 %.

DISCUSSION

Strain hardening is a welcomed event and should be taken into account in designing the modification

strategy. For a cohesionless array of particles and as soil goes into the critical state, recent discrete element numerical modelling attempts (see Jerves & Andrade 2015) infer that vorticity mechanisms furnish most of the particle-level kinematics. Here, flocs are believed to mobilise in between soil particles through one or a combination of three fundamental contact level vortex-like sub-mechanisms, namely sliding, rotation and rolling. In fact, contact points begin rotating or rolling as strain increases towards the critical state. The number of rotating/rolling contact points becomes maximum and stable at the critical state; this is a steady state at which the number of contacts that initiate or terminate sliding remain unchanged. As the flocs crush on further straining, the array of particles once again loses confinement and the soil enters a final phase of rapid strain softening.

The particle-level kinematics that control the macro-behaviour of modified peat specimens here provided an opportunity to gain new insights into the role played by silica flocs on the build-up of macro-mechanical quantities such as peak and critical state strength. Our findings are translated into the following suite of design recommendations for groundworks practice:

- Nanosilica treatment generally reduces the peak strain, increases the peak strength, and yields a brittle stress-strain behaviour.
- In the first 14 days, an increase in nanosilica load to 25 % in colloidal solutions yields lower residual strength as strain grows to 1.5 % plastic strain. In the long term, a 20 % nanosilica load appears to yield maximum residual strength.
- Whilst introducing colloidal solutions with the highest 30 % nanosilica load to peat soil offers the greatest peak strength, the residual strength at 1.5 % and 2 % peak strength falls to extremely low values for colloidal solutions of >20 % nanosilica load. This is greater than the recommended nanosilica content for improvement of other soil-based cementitious materials. For example, Haeri *et al.* (2015) reported a four times increase in the unconfined compressive strength of North East Iranian loess, 3 days after treatment of the loess with a modest 3 % by weight of nano-silica hydrosol. They reported only a marginal change in strength at greater nano-silica contents.
- A design 15–20 % nanosilica load in nanosilica solutions will yield reasonably high (66–68 kPa) compressive strength immediately after treatment and 160–175 kPa in 28 days. This is a rise in compressive strength from an initial 23 kPa and is

a satisfying improvement when compared with earlier attempts on peats of similar untreated unconfined compression strength (UCS). For example, Said & Taib (2009) reported an increase in UCS from 38 kPa to 115 kPa upon mixing peat with lime at 12 % by weight. The loss of strength on further straining is capped to 9 % at $\epsilon_{ri} = 1.5\epsilon_p$ and 73 % at $\epsilon_{ri} = 2\epsilon_p$. Caution needs to be taken against post-peak straining in the first seven days post treatment.

- The benefits of using the recommended 15–20 % design nanosilica load in colloidal silica solutions extend to spells of strain-hardening and hence relaxation of flow potential in the early days following treatment, when engineered ground is most susceptible to failure at high strains.

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AUTHOR CONTRIBUTIONS

Fieldwork and mechanical testing were performed by SG. AAL undertook and analysed the results of electron microscopy. SG and AAL jointly developed the analysis, interpretations and write-up with contributions from CH, who also coordinated the work to tie in with the wider studies in hand within the tenets of the funded project.

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