Stabilisation of peat with colloidal nano and micro silica

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SUMMARY

Peat occurs abundantly in wetlands across Iran, particularly around the disappearing Urmia Lake. Conventional chemical stabilisation has been widely used to tackle the high compressibility and shrinkage potential of peat. Whilst effective, this generally reduces the carbon storage capacity of peat. Exotic stabilisers such as nano-silica (NS) have been shown to be relatively less harmful and without any direct environmental risk. NS has proved effective in improving the mechanical properties (to some extent) and pH-dependent natural structure of peat, but is commercially nonviable. This article presents findings from an experimental study of Urmia Lake peat stabilised with composites of NS and cheaper micro-silica (MS). Unconfined compressive strength (UCS) and California Bearing Ratio (CBR) tests were conducted on untreated and treated compacted natural peat soil samples after 7, 14 and 28 days of curing. Nano-silica was varied from 3 % to 9 % (by dry mass) in 3 % increments and micro-silica was varied from 6 % to 24 % (by dry mass) in 6 % increments. The observations are explained in terms of micro-scale events using XRF spectroscopy and SEM imaging. The findings suggest that the UCS of peat can be increased by administration of NS-MS composites, and the effectiveness is dependent on the relative content and particle size of NS and MS. The UCS and elasticity modulus increase with curing time. As manifested in the CBR results, administration of the composites improves the bearing capacity of peat and transforms it into a sub-base with suitable engineering functions whilst safeguarding its ecosystem service provisions.

KEY WORDS: bearing capacity, carbon, CBR, nature-inspired, organic, soil, UCS

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INTRODUCTION

Peat soil contains more than 75 % organic materials and is formed when organic matter (usually vegetation) is conserved below a high water table in swamps or wetlands (Jarrett 1997, Warburton *et al.* 2004, Duraisamy *et al.* 2007, Xintu 2008, Kalantari 2013). As a non-mineral soft soil type, peat has very high organic content, low shear strength, very high moisture content, and high compressibility. These mechanical properties make peat a notoriously difficult material to build on in construction projects (Barden & Berry 1968, Hebib & Farrell 2003). For shallow peats, excavation, and substitution of peat with a stronger granular fill has remained a popular option (MacFarlane 1969). For deep peats - when the peat is buried - chemical stabilisation (Axelsson *et al.* 2002) and pile installation to transfer the load to harder strata are common engineering measures (Satibi 2009). Edil (2003) summarises several construction methods that can be applied to peat and organic soils, namely excavation and replacement, reinforcement, preloading, piling, thermal processing, and chemical stabilisation with cement and lime for enhancement of the strength and stiffness.

Peat deposits are patchily distributed across waterlogged upland and lowland environments in isolated but widespread parts of Iran. In north-western Iran, Lake Urmia (as a whole) has been designated a wetland of international significance under the 1971 Ramsar Convention on Wetlands. Peat can be found in abundance across a network of wetlands south of Lake Urmia (Amini *et al.* 2010), the Golmarz Wetland some 8 km east of Urmia City (Badv & Sayadian 2012), and along the Urmia-Tabriz highway towards the eastern shores of the lake. This peat soil is capped with about 40 cm of terrigenous deposits which are slightly clayey, slightly calcareous, medium to coarse sand soils transported into the lake by local rivers and northerly flows. Amini *et al.* (2010) summarised the mineralogical composition of this drift as a mixture of quartz, feldspar, calcite, ash, pyroxenes, mica, ferric sulphides, organic matter and phyllosilicates. As a result, the Urmia Lake region is notorious for its challenging ground conditions, especially in relation to the need for arterial roads to pass through the area. Local challenges arise in the form of long-term creep settlement; that is, long-lasting ground subsidence under constant load, which was seen during

construction of the Urmia Lake overcrossing (see Figure 1). The overcrossing forms the first two phases of a national infrastructure project to construct a highway that will reduce the travel distance between Tabriz megacity and Urmia by 100 km. The highway development project has six phases. At the time of writing, the third phase of the project consisting of roadworks on Islami Island (previously King Island) - a wetland conservation area - is underway and developments east of the lake to Tabriz are yet to begin. The construction began in 1980 with erection of rockfill embankments that advanced into the lake from both sides. Only 14 km of the planned 22 km total length of embankment was completed by 1989, when the project went into deadlock owing to excessive ground subsidence. A combination of erosion and progressive creep settlement of organic lakebed soils was blamed for failure of the development. The contingency adopted in 1989 was the construction of a cable bridge to connect the two rockfill embankments; however, the bridge lasted only four months due to the instability of abutments. A new 1.4 km long bridge was constructed between 2004 and 2008, but creep settlements continued to cause disorientation of bridge abutments and, consequently, a range of structural defects (Badv & Sayadian 2012). Such creep settlement of peat has been reported widely across the globe, in Ireland (Hebib & Farrell 2003, Reilly & Buggy 2022), Italy (Gambolati *et al*. 2006), Wales (Nichol & Farmer 1998), Malaysia (Marshall *et al.* 2018), Ghana (Attoh Okine 1992), Canada (Samson & Rochelle 1972) and New Zealand (Pronger *et al.* 2014). Mechanisms leading to the problem were discussed in the pivotal study of Mesri *et al.* (1997).

In order to identify an effective stabilisation measure, one needs to have a thorough understanding of the properties and failure mechanisms of peat. The links between its mechanical and physical properties remain a matter for research, although the poor mechanical response has been broadly attributed to its pH-dependent structure (Šķēls *et al*. 2013). The physical properties of peat depend upon the four major components of the organic soil system, namely the organic material, the mineral material, water, and air. An effective stabilisation measure needs to take account of, and be tailored to, these four major phases, as well as to satisfy three requirements: affordability, adaptability (to the natural environment), and long-lasting mechanical effectiveness. This creates a demand for new stabilisation methods (Puppala & Musenda 2000).

Of the conventional chemical additives, lime and gypsum are reasonably inexpensive and accessible, cement appears to be rather effective, and all of these

change the pH balance of peat causing carbon efflux. However, it is important to understand the extent to which mechanical properties of peat can be improved by conventional stabilisers. According to ASTM D4609-94e1 (standard guide for evaluating the effectiveness of admixture for soil stabilisation), soil stabilisation is deemed effective if it increases the unconfined compressive strength (UCS) to at least 345 kPa (Sariosseiri & Muhunthan 2009). Kolay & Pui (2010) indicated that when 6 % gypsum by mass was added to peat soil, the unconfined compressive strength (UCS) increased from 6.5 kPa to only 44.94 kPa, whereas Said & Taib (2009) reported a somewhat greater increment in UCS from 38.3 kPa to 115.5 kPa as a result of adding 12 % by weight of lime.

Colloidal nano-silica (NS) hydrosol is a novel alternative stabiliser that has recently been used in stabilising sands (Ghadr *et al*. 2020a), loams (Krishnan & Shukla 2021) and clays (Changizi & Haddad 2017). NS has been used as an additive in the concrete and insulation industries for over 30 years but has never been used in large-scale stabilisation of peat. Indeed, there have been very few previous attempts to use silica-based binders to stabilise peat at any scale. When added to peat, NS meets the environmental adaptability requirement, contributes to the transformation of natural peat into an engineered subbase, and is relatively accessible. Ghadr *et al*. (2020b) recently studied NS-stabilised peat in terms of UCS and the particle-level kinematics that control the macro-behaviour. They specifically discussed the role played by silica flocs on the build-up of macro-mechanical properties such as peak and critical state strength. From a microstructural viewpoint, they presented scanning electron microscope (SEM) images showing that silica polymerises to form coagulated units or flocs (globules) in the soil solution. Flocs form 'trapdoors' in the necks of soil pores. At early stages, and whilst polymerisation is still ongoing, the platy texture of the silica globules results in rapid rearrangement of particles and turmoil in both fabric and interparticle forces, which manifests itself in the form of clearly visible jigsaw fluctuations in stress-strain response. In fact, increasing NS content to 25 wt.% (or 30 wt.% NS hydrosol) compromises the residual strength in the first 14 days. The problem eases with curing time, yielding the maximum residual strength at 20 wt.% NS content. Overall, NS treatment generally reduces the peak strain, increases the peak strength, and yields a brittle stress-strain behaviour. A design load of 15–20 wt.% NS in colloidal solutions will yield reasonably high (66–68 kPa) compressive strength immediately after treatment and 160–175 kPa in 28 days (Ghadr *et al*. 2020b).

Figure 1. Location and morphological setting of Lake Urmia, Iran (Global Digimap ®).

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In comparison with conventional additives, NS is typically 6–10 times pricier, which will be an economic barrier to its widespread utilisation. Micro-silica (MS; also known as silica fume) is on average 25 % cheaper than NS. This substantially lower cost prompts the question of whether a composite of MS and NS could be an effective alternative stabiliser for peat which is environmentally friendly and adaptive, with greater potential for economic viability. MS has been used for stabilisation of soft clays (i.e., inorganic compressible soils), as a standalone (Kalkan & Akbulut 2004) and in combination with cement (Li *et al*. 2021). These studies showed that 20 % MS in clay can reduce the swell-shrink potential (also the liquid limit and plasticity index) but results in a lower maximum dry density and a higher optimum moisture content. More recently, Badv & Emdadi (2016) showed that the addition of 5–30 % MS increased the plasticity index of soil but had no clear effect on compaction properties. They also reported findings from a programme of unconfined compressive tests on Nazloo Clay stabilised with 30 % MS, which yielded a 69 % increase in undrained cohesion. These are conflicting but interesting findings because, in the context of peat, the presence of a clay (phyllosilicate) fraction is almost certain. The use of MS-lime mixtures for soil treatment has also received some interest. GhavamShirazi & Bilsel (2021) referred to pozzolanic reactions with silica from MS and calcium from lime, and implications in treating expansive clays. They recommended using 10 % MS and 3 % lime mixtures for remediation of expansive clays. Karimi *et al*. (2011) studied the effect on California Bearing Ratio (CBR) of adding combinations of MS and lime to silty sand road and railway subgrade. They showed a general rise in CBR for a MS content of up to 10 % and reported that higher contents of MS have compromising effects. For sulfate silty sands (containing 25 wt.% $CaSO_4.2H_2O$), Ghorbani & Hasanzadehshooiili (2018) recommended using 2.5 % MS and 1.5 % lime mixtures, employing CBR as an index for soil strength.

Common to all previous studies is the low emphasis on chemical interactions at particle level. To the best of the authors' knowledge, no attempts to use an entirely silica-based NS-MS grout have been made and published to date. Such a grout, if confirmed effective, would have a low carbon footprint - as compared with cement and lime, or NS/MS mixed with alkali-activators - and would be financially more feasible. Both MS and NS are globally abundant; and their administration in soils, particularly ecologically sensitive organic soils, would be more compatible with ground's natural ecosystem.

At large scale, the thickness of the peat layers west of Lake Urmia can be up to 6–8 m. Removing the peat and replacing with gradual fill is a comfortable practice that is already adopted as the principal engineering solution. In this article we introduce the idea of removing only the top 1–2 m of peat (depending on the bearing capacity requirement), mixing that top peat layer with a mixture of NS-MS, compacting in-situ and reinstating the ground to provide the engineering bearing capacity needed. This approach will have a 'relatively smaller' negative impact on the underlying and surrounding peat, and will avoid the prospect of removing the peat sequence altogether. In the research reported here, we investigate the performance of an NS-MS grout in stabilising Lake Urmia peat. To enable direct comparison with results previously obtained for NS alone, we utilise the same peat and NS materials as Ghadr *et al*. (2020b) with the addition of MS, and follow their methodology for determination of UCS. Additionally, we determine CBR. The micro-structural basis is then explored using SEM.

METHODS

In outline, colloidal NS solutions (3 %, 6 % and 9 % by weight) and MS powder (6 %, 12 %, 18 % and 24 % by weight) were added to the base peat soil, then the mixtures were compacted at optimum water content and cured under controlled ambient conditions for three different curing times (7, 14 and 28 days). Thirty-seven UCS and twenty CBR tests were conducted, each repeated three times to accommodate the exceptionally high variability of properties in organic soils, and the fundamental dependency of failure plane - and hence strength and strain at peak - on the quality of compacted UCS specimens. Further details of the materials and procedures are provided below.

Urmia Lake peat
The testing material was the natural highly organic soil obtained from the Urmia–Tabriz–Shahid Kalantary Highway, east of the city of Urmia in Iran (Figure 1) previously tested with NS stabiliser by Ghadr *et al*. (2020b). It is a highly organic soil rather than pure peat. The terms 'peat' and 'peat soil' are used interchangeably throughout this article. Figure 2 shows the landscape of the study site and a peat exposure.

Figure 2. The sampling site in pictures: (a) view to the north; (b) marshlands on alluvium overlying peat; (c) marshlands meeting the precipitated salt on the lakeshore; (d) exposed peat. Photos: A. Assadi-Langroudi, (d) (only) reproduced from Ghadr *et al*. (2020b).

Samples were obtained from the bottoms of five 1.5 m deep open trenches drilled at 6 m intervals in late spring 2019, when the peat was moderately wet. The extracted peat was dark brown in colour, spongy, and classified as H5 on the von Post scale (von Post 1922). The peat samples taken from the trenches were mixed to obtain a uniform base material for the tests described here as well as for those reported by Ghadr *et al.* (2020b). Various characteristics of the extracted material are provided for reference in the Appendix (Table A1).

Nano- and micro-silica hydrosol
Colloidal nano-silica (NS) and micro-silica (MS) are amorphous, negatively-charged materials that, unlike crystalline silica, lack long-range order. They can be found in natural form within the clay-sized fraction

of cemented soils and in low concentrations in groundwater (Loiselle *et al.* 1971). For this study, NS and MS were supplied in kind by ISATIS Silica Group (Yazd, Iran). Tables 1 and 2 summarise the physical and chemical properties of the NS and MS. The nano-silica 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, almost similar density to water (1.1 g cm^{-3} at 20 °C) and an average particle size of 16 nm. The MS was supplied as powder. The two materials were used to prepare twelve NS-MS suspensions.

Distilled water was added to the NS hydrosol to form 3 %, 6 % and 9 % (by weight) grades of NS suspensions. To reduce the repulsive forces between the NS particles (these arise from the negatively charged surfaces of silica particles) an accelerator

Table 1. Physical properties of MS determined in this study. Corresponding values for NS (*) from Ghadr *et al.* (2020b) are provided for comparison.

Properties	MS	NS*
Purity (%)	99	99
Average particle size (nm)	<200	16
Specific surface area ($m^2 g^{-1}$)	14–20	600–875
Bulk density ($g.cm^{-3}$)	0.2	0.1
Real density ($g.cm^{-3}$)	0.6	2.4
Colour	light grey	white

Table 2. Elemental analysis for colloidal NS and MS. LOI = loss in dry mass on ignition at 440 °C. Corresponding data for NS (*) from Ghadr *et al.* (2020b) are provided for comparison.

Component	MS fraction: wt.%	Colloidal NS fraction: wt.%*
SiO_2	85	33.96
Fe_2O_3	2	0.07
Al_2O_3	1	0.27
Na_2O	-	5.02
Cl	-	0.35
P_2O_5	-	0.11
CaO	1.5	0.07
MgO	2	0.046
SO_3	-	0.097
K_2O	-	0.12
C	3	-
LOI	5.5	59.89

was added to the suspensions to trigger 'jellification' and facilitate the formation of Si-O-Si bonds. The suspensions were then mixed with sodium chloride (NaCl) electrolyte and an aqueous solution of hydrochloric acid (HCl). This led to the collision of solid particles, formation of siloxane bonds, rapid polymerisation, and reduction of pH to 6. The gel time (i.e., the time required for the viscosity to increase above 1 cP) is generally a function of the ratio of colloidal silica to accelerator, and was adjusted through trial and error to be about 570 ± 20 minutes at 21 °C. This is generally consistent with previous attempts by other researchers (Agapoulaki & Papadimitriou 2015). The silica solutions were finally given 24 hours of curing time to set.

Specimen preparation and test procedures
The natural peat soil was transferred from the study site to the laboratory, stored, sieved, compacted, mixed, moulded and wrapped to form the test specimens as described by Ghadr *et al.* (2020b) except that, for chemically modified samples, the adjusted NS solutions and MS powder were added to the wet peat before mixing. Specimens were taken from storage in the environmental chamber at 20 ± 1 °C for mechanical testing on the 7th, 14th and 28th days.

Series of strain-controlled UCS and CBR (unsoaked) tests were carried out in compliance with the ASTM D2166 / D2166M–16 (UCS) and ASTM F1883-16 (CBR) standards. Curing time for CBR test specimens was limited to 7 and 28 days. To address the high variability of UCS and CBR values arising from the unconfined loading of the soils, each loading experiment was repeated three times on identical specimens to determine the average 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. The peak and post-peak responses were captured and illustrated in the form of stress-strain curves.

Test samples were prepared for and examined by Scanning Electron Microscopy (SEM) as described by Ghadr *et al.* (2020b).

RESULTS

Stress-strain behaviour
Table 3 summarises the test results, reporting UCS (peak unconfined compressive strength), elasticity modulus and CBR as strength and stiffness index parameters. The 7-day, 14-day and 28-day UCS values at different stabiliser contents are presented in Figure 3. Considerable changes to mechanical indices occurred as the NS and MS values changed in composite materials. Figure 3 shows that the strength of peat mixed with 3 % NS and 6, 12, 18 and 24 % MS increased, following a 7-day curing time, by 400, 275, 251 and 167 %, respectively, compared with untreated peat compacted to identical optimum conditions. For the higher NS content of 6 % the increase in peat strength was 363, 290, 236 and 174 % for MS contents of 6, 12, 18 and 24 %, again after seven days of curing. A further increase of NS

Table 3. Testing itinerary and results. UCS = unconfined compressive strength; E = elasticity modulus; CBR = California Bearing Ratio.

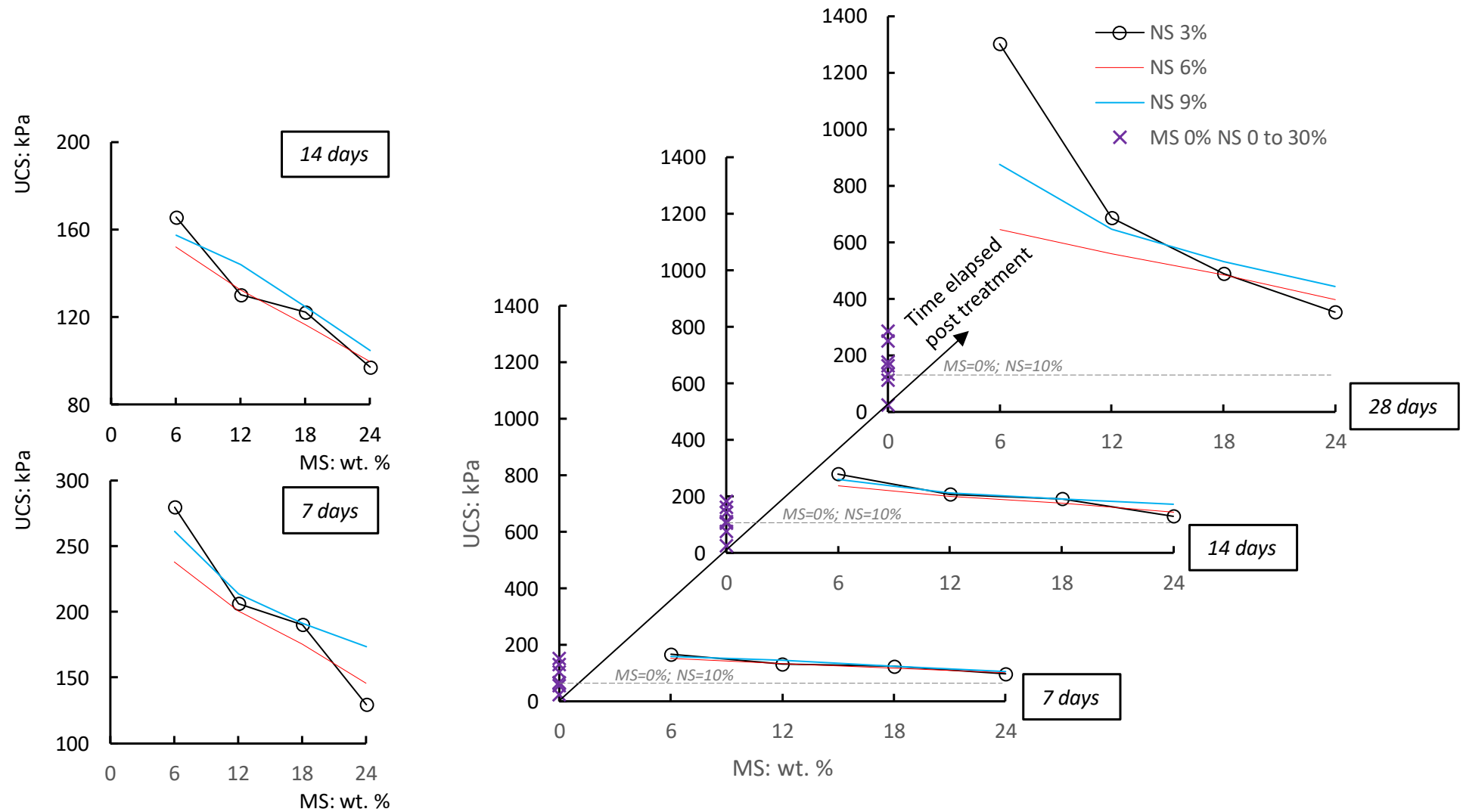| Test number	NS (%)	MS (%)	Curing time (days)	UCS (kPa)	E (kPa)	CBR (kPa)
1	0	0	7	32.50	1035.03	26.18
2	3	6	7	165.60	4224.49	78.20
3	3	12	7	130.20	3616.66	71.25
4	3	18	7	122.20	4364.28	66.35
5	3	24	7	97.12	3132.25	-
6	6	6	7	152.20	4712.07	73.58
7	6	12	7	132.40	3928.78	66.30
8	6	18	7	116.40	3516.61	60.12
9	6	24	7	99.52	2531.80	-
10	9	6	7	157.50	4500.12	76.24
11	9	12	7	143.80	3994.44	68.35
12	9	18	7	124.60	4019.35	63.41
13	9	24	7	104.60	3076.47	-
14	3	6	14	279.60	4820.69	-
15	3	12	14	206.20	4043.13	-
16	3	18	14	189.90	3452.72	-
17	3	24	14	129.50	4046.87	-
18	6	6	14	238.14	5670.42	-
19	6	12	14	200.52	6076.36	-
20	6	18	14	175.55	5148.09	-
21	6	24	14	145.39	3929.45	-
22	9	6	14	261.29	5559.36	-
23	9	12	14	213.42	4446.25	-
24	9	18	14	191.58	5473.71	-
25	9	24	14	173.61	3100.17	-
26	3	6	28	1300.51	22042.54	155.36
27	3	12	28	685.26	14276.25	143.69
28	3	18	28	488.03	7871.45	125.69
29	3	24	28	353.57	7215.71	-
30	6	6	28	644.31	16955.53	136.17
31	6	12	28	560.31	10569.25	127.36
32	6	18	28	485.23	11608.13	117.68
33	6	24	28	396.15	8611.69	-
34	9	6	28	876.12	14602.36	146.32
35	9	12	28	646.06	11964.07	132.58
36	9	18	28	530.39	12509.20	118.69
37	9	24	28	443.27	8524.42	-

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Figure 3. Lake Urmia peat with micro silica (MS) and nano silica (NS) additives: variation of unconfined compressive strength (UCS) with additive levels and time elapsed post treatment.

content to 9 % led to an increase in peat strength by 375, 330, 254 and 185 % after seven days of curing, for the same series of MS contents.

Curing time has a substantial effect on the strength of treated peat samples. When the curing time was increased to 14 days, the strength of peat mixed with 3 % of NS and 6, 12, 18 and 24 % of MS increased by 811, 552, 495, 280 %, respectively, compared with untreated peat compacted to identical optimum conditions. Raising the NS content to 6 % increased peat strength by 661, 531, 443 and 336 % for MS contents of 6, 12, 18 and 24 %, and raising NS content to 9 % increased peat strength by 746, 573, 499 and 437 % for the same series of MS contents.

The data show a direct relationship between the setting (curing) period and UCS. Regardless of curing time, the UCS initially decreases with an increment of NS from 3 % to 6 %, and then increases with further increase of NS to 9 %. A similar pattern can be seen in gain-in-UCS upon stabilisation. In Figure 3, the data from this investigation are combined with the earlier findings of Ghadr *et al.* (2020b), for NS ranging from 0 % to 30 % in 5 % increments. It was established by Ghadr *et al.* (2020b) that UCS correlated directly with NS content in the peat. Four key immediate observations from Figure 3 are:

1. Comparing UCS values in the absence and presence of MS infers that MS substantially improves the compressive strength of peat.

2. Small increments of MS content cause large losses of UCS. Despite the loss, the overall UCS of peat with MS remains greater than for peat without MS, at any given NS content.

3. The trend of loss in UCS with incremental increases in MS rapidly loses momentum at higher MS contents.

4. The addition of MS to the peat disturbs the direct correlation between NS and UCS previously reported by Ghadr *et al.* (2020b), except in the case of peat mixed with the highest tested concentration (24 wt.%) of MS. This implies an interference of MS polymerisation with the NS thin films that cover mineral- and organic-based particles.

With a further increase in curing time to 28 days, the strength of peat mixed with 3 % NS and 6, 12, 18 and 24 % MS increased by 4422, 2242, 1548 and 1073 %, respectively, compared with untreated peat compacted to identical optimum conditions. When compared with the levels seen after 7-day and 14-day setting times, the findings indicate an exponential increase in UCS. At the higher NS content of 6 %, the increase in peat strength was 2101, 1807, 1535 and

1223 % for MS contents of 6, 12, 18 and 24 % after 28 days of curing, and increasing the NS content to 9 % led to peat strength increasing by 2921, 2107, 1698 and 1391 % for MS contents of 6, 12, 18 and 24 %. Similar to the observations of 14-day data, the findings here show that UCS decreased sharply when NS content was increased from 3 % to 6 %, then increased slightly with further increase in NS content from 6 % to 9 %.

Figure 4 presents the test data obtained for unsoaked CBR. CBR reached its maximum value in peat stabilised with 3 % NS and 6 % MS, showing increases of 78.2 % and 155.4 % after 7 and 28 days of curing, respectively. The CBR values decreased as MS content increased. Consistently with the UCS data presented above, CBR increased with curing time. The addition of 3 % NS increased CBR, while further increments of NS led to an initial decrease in CBR, followed by an increase at higher NS contents.

Large strain stiffness

Modulus of elasticity (E) in soils is directly associated with the elastic (immediate) settlement. The UCS test provides this value for elastic materials; whereas in elasto-plastic soil behaviour, modulus of elasticity (E) and Poisson's ratio (ν) are typically derived through triaxial shear testing. Figure 5 shows that the secant elasticity modulus (E) of improved peat with the lowest amount of stabiliser (peat soil + 3 % NS + 6 % MS) increased by 300 % at 7 days post-treatment. The highest (350 %) and lowest (119 %) increments of E after seven days of setting appeared in peat soil treated with 6 % NS + 6 % MS and 9 % NS + 24 % MS, respectively. Similar to UCS, stiffness was directly associated with setting time. In most cases, samples with 12 % MS yielded the highest values of elasticity modulus. In peat mixed with the lowest amount of stabiliser (3 % NS + 6 % MS), E increased by 393 % after 14 days. The highest (500 %) and lowest (200 %) increments of E after 14 days of setting appeared in peat soil treated with 6 % NS + 12 % MS and 9 % NS + 24 % MS, respectively. Samples with 3 % NS mixed with 6 % and 12 % MS showed higher E values than those blended with 18 % and 24 % MS. In peat mixed with the lowest amount of stabiliser (3 % NS + 6 % MS), E increased by 2306 % after 28 days. The lowest E value (652 % after 28 days of setting) appeared in peat combined with 3 % NS + 24 % MS. Elasticity modulus increased with curing time. For example, the secant elasticity modulus (E) of peat soil mixed with 3 % NS and 6 % MS increased by 500 % at 28 days compared to the 7-day secant elasticity modulus. Overall, these results show that the addition of NS and MS to peat soil generally improved the
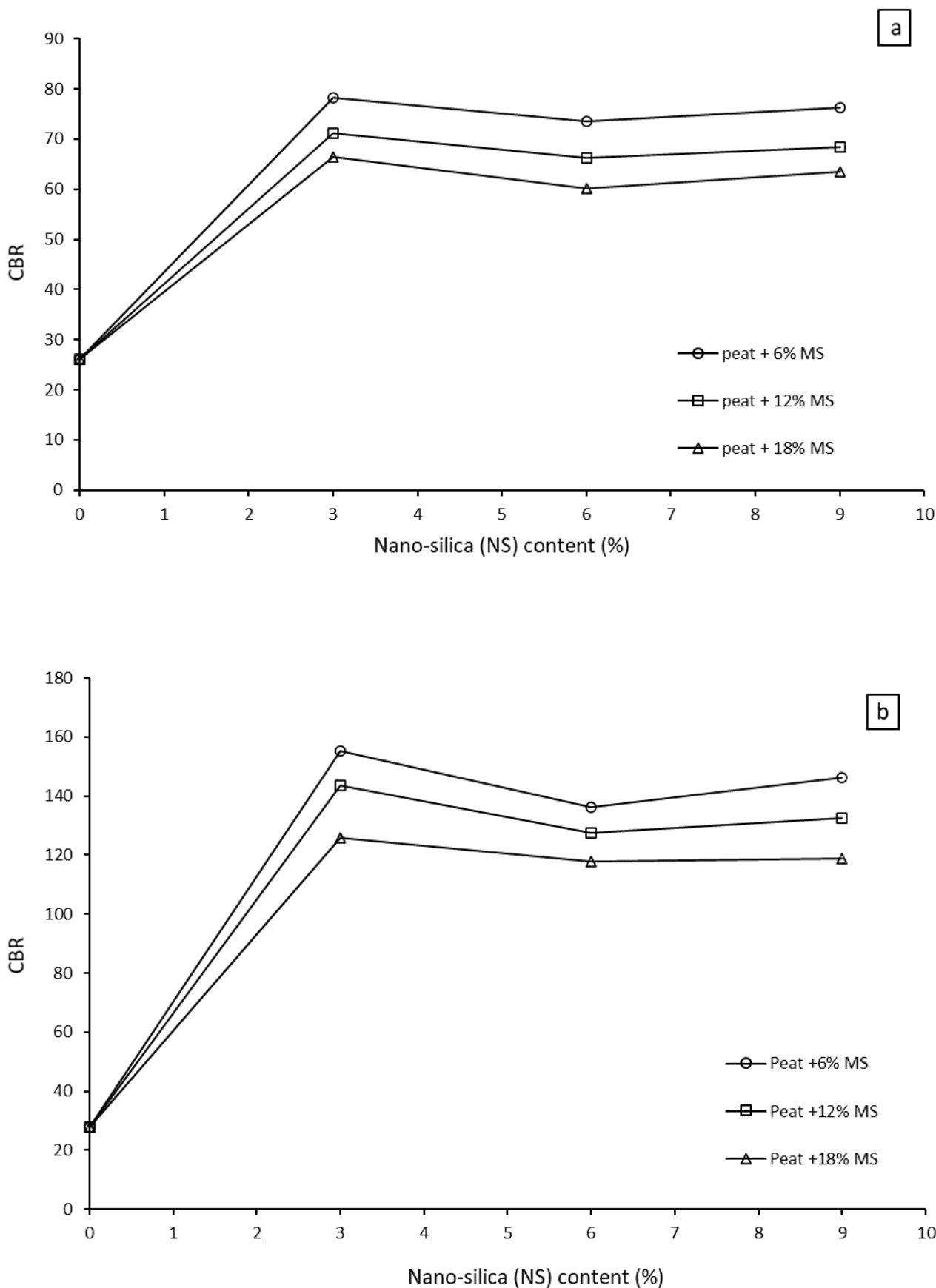
Figure 4. California Bearing Ratio (CBR) of peat soil stabilised with NS and MS, after curing times of (a) 7 days and (b) 28 days.
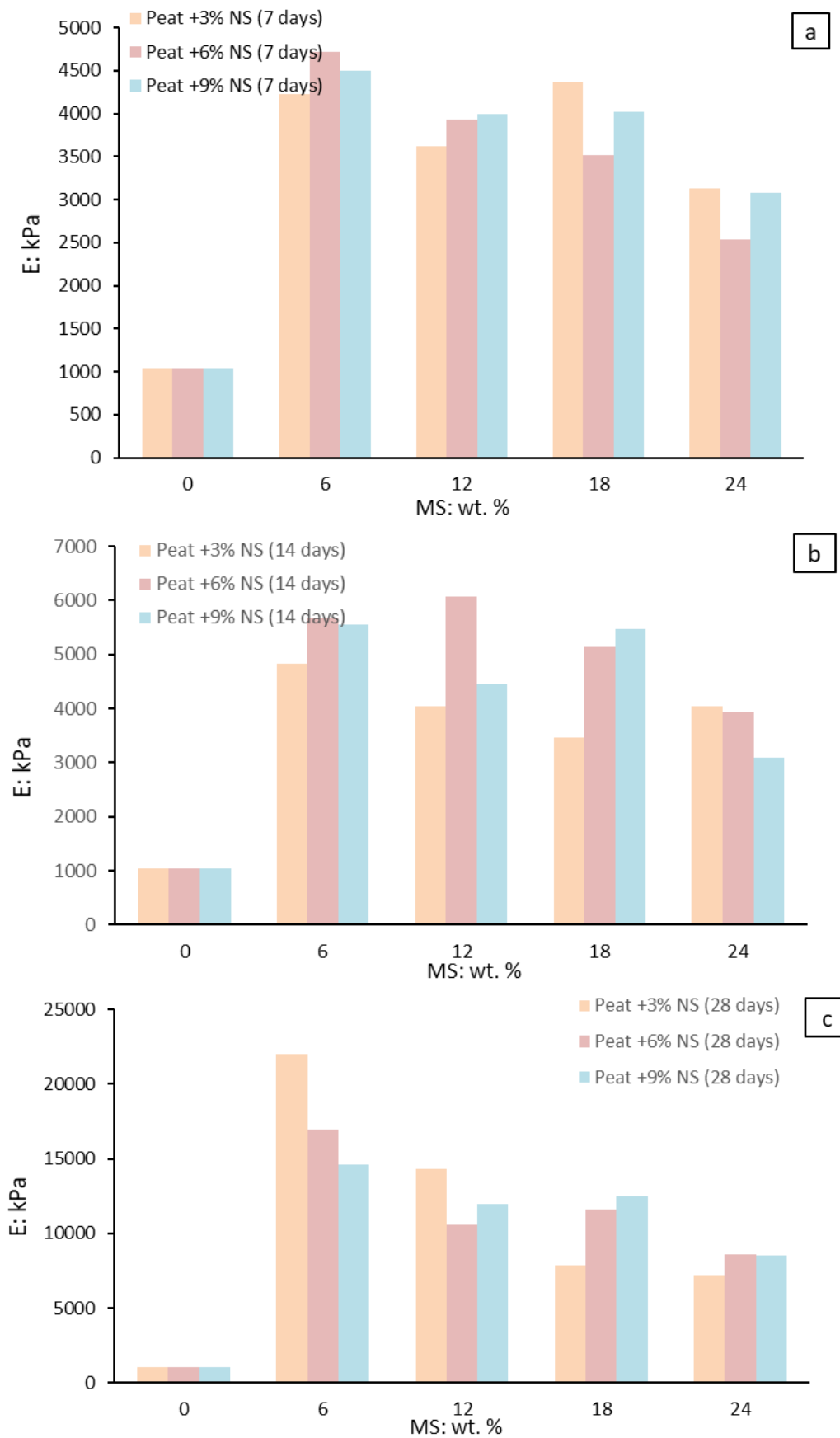
Figure 5. Elasticity modulus of peat soil stabilised with NS and MS after curing times of (a) 7 days, (b) 14 days and (c) 28 days.

modulus of elasticity, and the improvement increased with curing time. The effectiveness of the improvement appeared to be long-lasting.

Micro-scale insights from SEM

Table A1 summarises physicochemical properties of the base peat soil. The chemical properties (obtained by X-ray fluorescence spectroscopy for a subset of less-organic samples) imply that the coatings seen in the scanning electron micrograph in Figure 6a are most probably of a polymineral nature, consisting of ferromanganese, hydrous iron oxides, silica oxides and colloidal ferric oxides. Such a composition will have implications in the presence of added nanosilica, as will be discussed in detail later. Two micrographs of NS treated peats are shown at identical magnifications in Figures 6b and 6c. It is worth noting that the soil specimens were oven dried during preparation for scanning electron microscopy and were thus inevitably dehydrated and underwent considerable shrinkage. Because of this, clay and organic platelets are expected to appear less rounded, with sharp edges (see the clay platelet marked in Figure 6a). In Figures 6b and 6c, the general morphology consists of plate-like units with smooth texture and curved edges. The soft, discrete texture is the signature of layers of colloidal silica that coat crystalline particles and fibres, or even silica flocs that are constituted of tightly packed silica globules (Figure 6c). In either case, silica coating units exhibit satisfyingly low rates of solubility because the aluminium and magnesium ions in the base peat join them to form complex protective silicate shields (see Figure 6f and remarks in Xia & Han 2009).

The basic structure of peat soils is formed by a core of clay platelets and organic fibres, both identifiable in Figure 6a. There is a fundamental difference between NS and MS morphologies. The former appears as a coating on particles (Figure 6b) and also as flocs (Figure 6c) that constitute fine 1 µm and sub-1µm rod-shaped silica globules. The latter has the appearance of small and larger pellets, either scattered across soil particles or joined together in loose honeycomb structures (Figure 6d). The open structure can be attributed to the rigid wall boundary effect; that is, the relatively larger mean size of mineral-based particles and organic fibres leads to highly porous MS assemblages in their immediate vicinity (Figures 6d and 6e). As MS content increases, some MS pellets relocate to the intra-lattice pore spaces to form dense assemblages; these can be seen in between larger particles/fibres or in the necks of pore spaces (Figure 6g). These dense assemblages facilitate the movement of surrounding larger particles; they act as *fulcrum*, encourage

particle displacement and compromise the overall strength. This effect is visible in Figures 6g and 6h, which shows two marked rounded dense assemblages of MS pellets in between mineral-based assemblage units, all within the porous structure of the peat soil.

DISCUSSION

Micro- to macro-insights

The core structure of peat at micro-scale is porous plant cellular matrix structures which are linked together via larger organic fibres that are relatively less decayed (O'Kelly 2015). These open cellular structures are mostly not visible in Urmia peat samples on account of their high mineral content (clay and some quartz) and the disturbed state of retrieved soil specimens. Whilst the mineral component of Urmia peat shears at frictional contacts, the organic component fails through tearing of the porous organic cellular mesh and fibres that connect the meshes. In Ghadr *et al* (2020b), the direct correlation between NS and UCS implies a role of colloidal silica in filling the open cellular structure, coating connecting fibres and shielding the clayey assemblages, which increases the resistance against erosion, the liquid limit and hence the structural integrity. Four important observations are made here:

i. Irrespective of their content, MS pellets act as keys and add to the soil a degree of frictional resistance that does not exist otherwise. This is manifested in greater UCS values in peat soils containing MS (Figure 6g).

ii. In (low) concentrations of 5–10 wt.%, MS pellets are loose, often scattered, and provide relatively high specific surface. On introduction to the soil, NS initially tends to attach to MS surfaces (the mechanism is explained at the close of this section) and provide onion-skin coating (Figure 6f). On completion of coating, the excess NS moves to the intra-lattice surfaces of organic meshes. This is evident in Figure 3; increasing NS content from 3 to 6 wt.% leads to a substantial loss in UCS. The scattered and loosely spread MS pellets are coated with colloidal nanosilica, thus gaining smoother surfaces and a capability to roll which compromises the overall peat strength.

iii. In (moderate) concentrations of 10–20 wt.%, MS pellets begin to join and form denser, rounder, larger aggregates in between organic and mineral sheets. The denser packing results in lower specific surface. This explains the far gentler loss in UCS upon increasing NS content from 3 to 6 wt.%. Colloidal nanosilica partially coats the MS
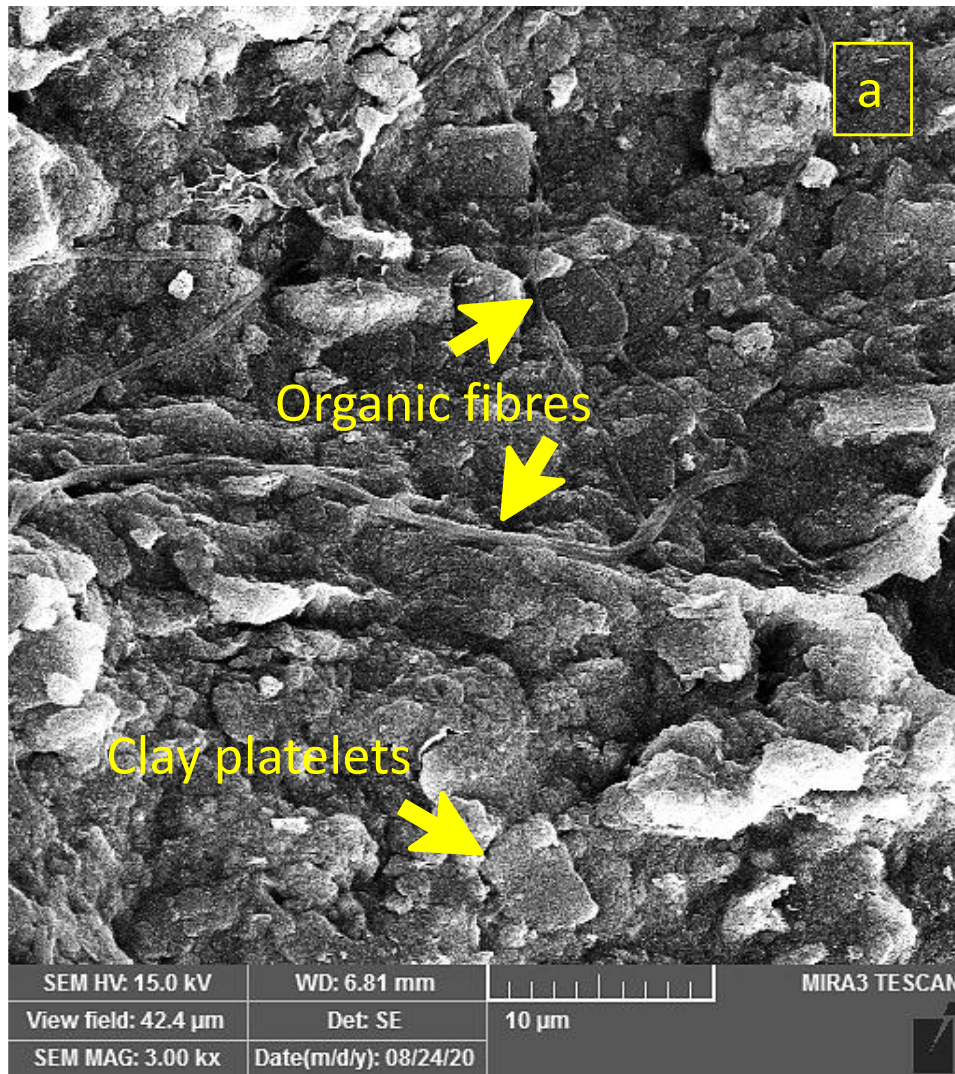
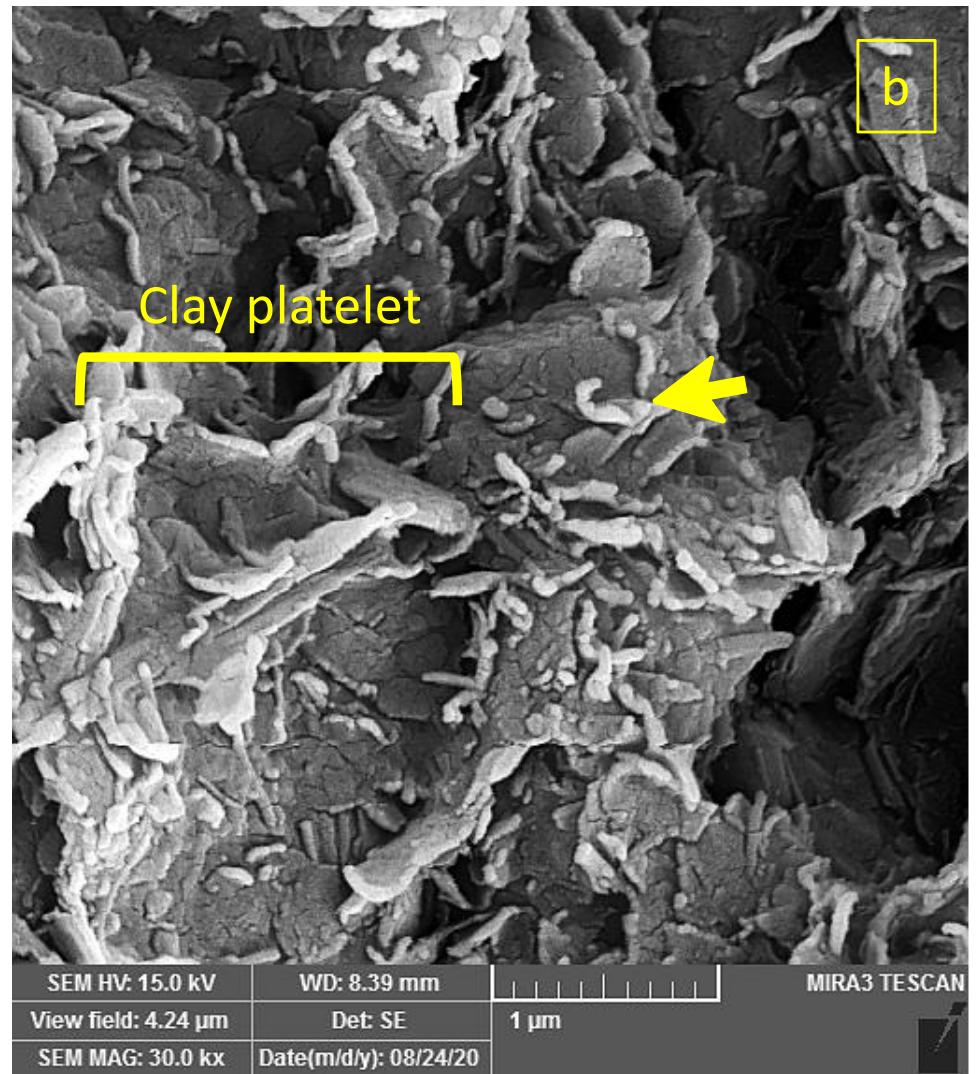Figure 6a. Clay platelets and organic fibres from the base soil, covered with polymineral coating units.

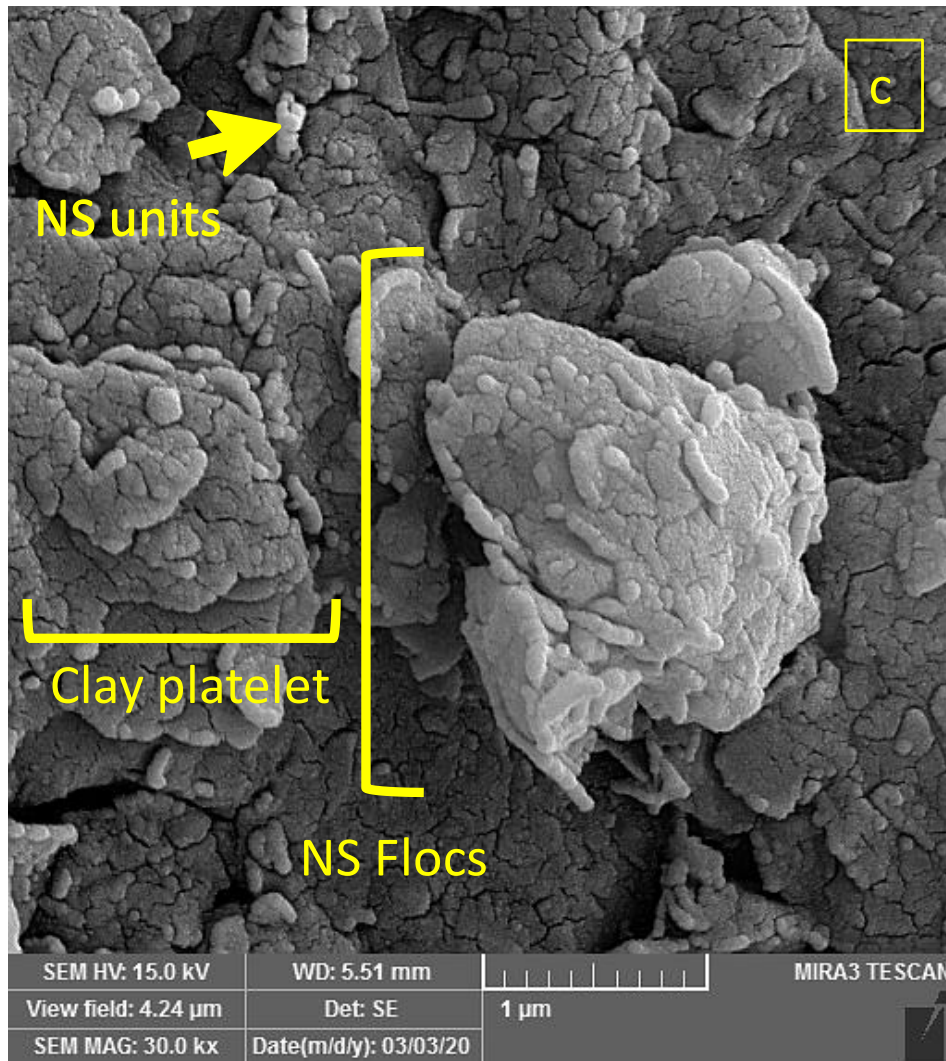Figure 6b. NS treated peat: 1 µm and sub-1µm rod-shaped NS globules on clay platelets.

Figure 6c. NS treated peat: NS flocs and heavily coated clay platelets with colloidal silica forming smooth, rounded, closely-packed NS globule units.
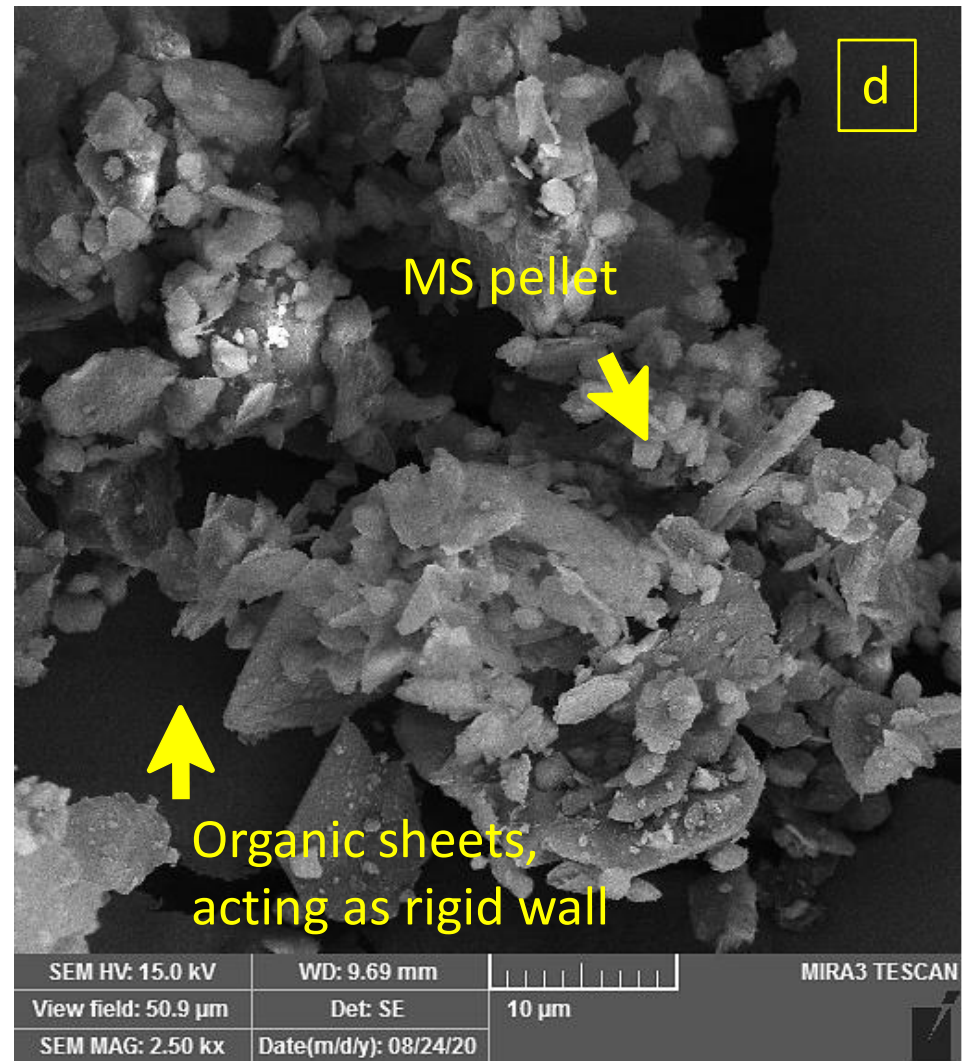
Figure 6d. MS treated peat: small and larger MS pellets in loose honeycomb structures next to larger mineral-based and organic rigid surfaces.
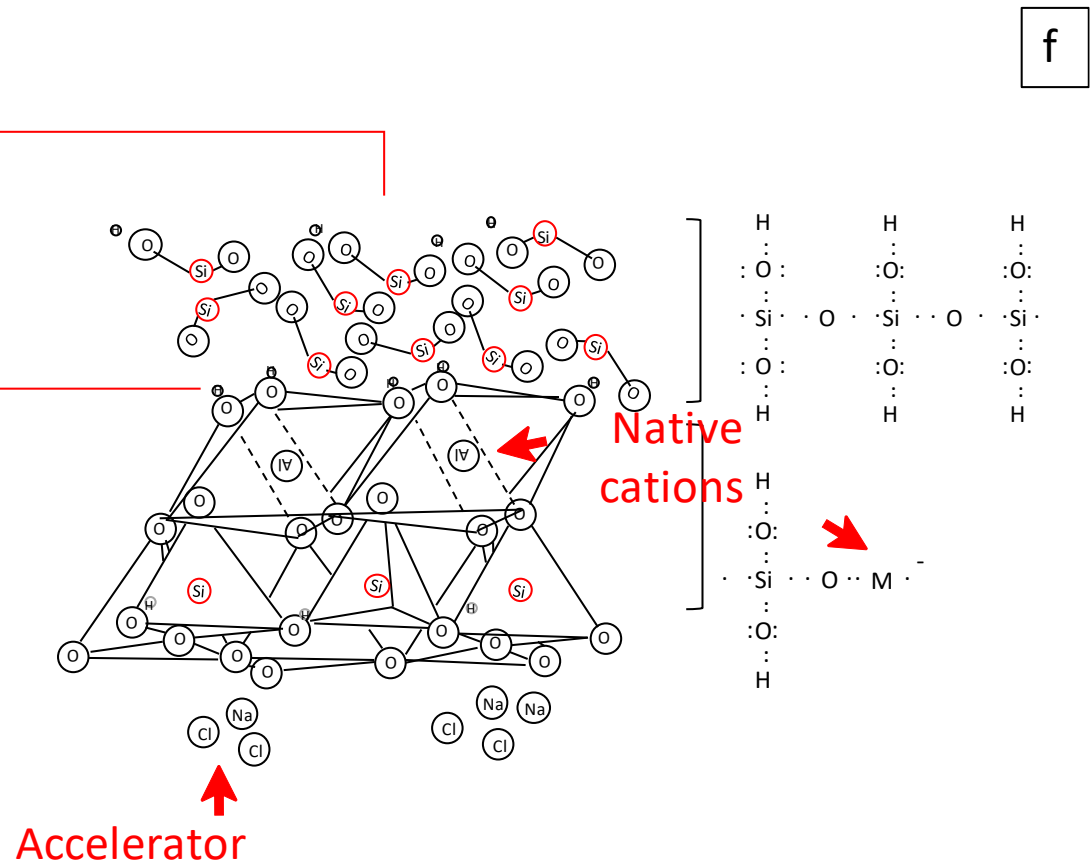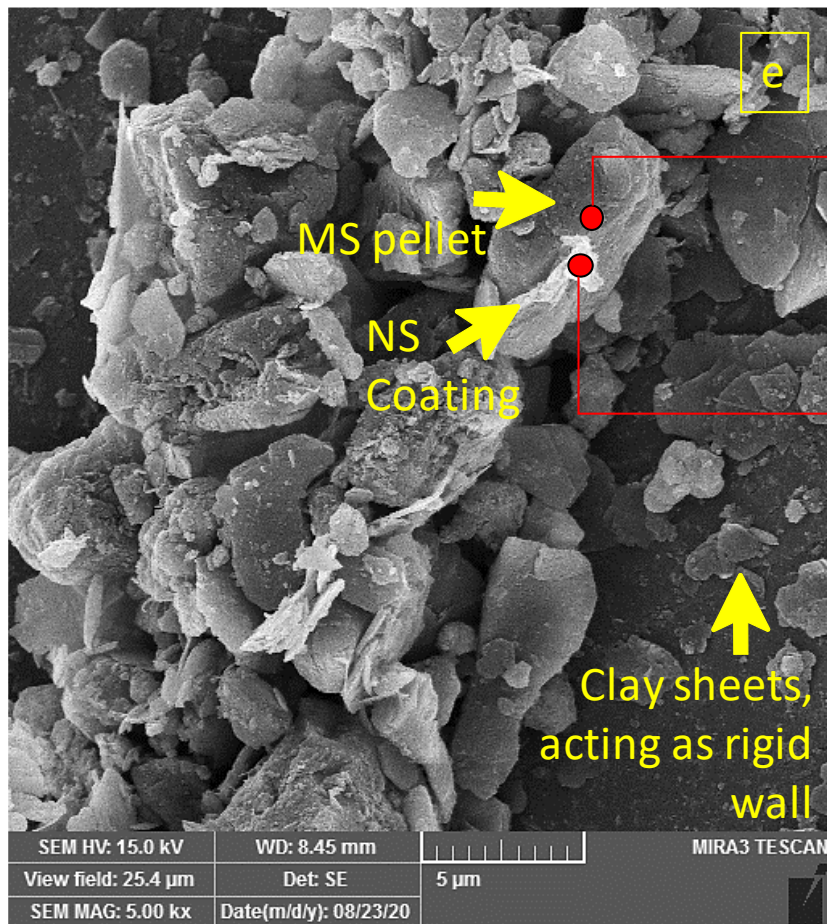
Figure 6e. Rigid wall effect yielding a loosely packed structure of MS pellets.

Figure 6f. Interaction of silica from NS with Al and Mg ions in base peat resulting in formation of less-soluble silicate shields.

pellets and the excess, immediately, goes to the intra-lattice space of organic meshes.

iv. In (high) concentrations of ≥25 wt.%, MS pellets are already accumulated into densely packed silt-sized aggregates. This begins to change the overall behaviour of peat soil from purely cohesive to frictional. Relatively little content of colloidal nanosilica is needed to coat the relatively small specific surface of MS aggregates and the rest goes to the intra-lattice spaces of organic meshes. This is evident in the direct correlation between NS and UCS illustrated in Figure 3.

Assadi-Langroudi (2014) showed that silicon cannot practically share covalent bonds and hence carries a net negative charge, which allows it to participate in chains of Si-O-Si. The XRF profile of the base peat soil reveals that, in untreated peat, small amounts of Fe^{3+}, Al^{3+} and Ca^{2+} coexist with Si^{4+} and organic matter. These are potentially bonding ions that enter the amorphous phase and build chains of amorphous silico-alumina. Each chain has a core of amorphous silica, consisting of silicon in tetrahedral coordination, and a coating in octahedral coordination resulting from some isomorphic substitution of Si with Al. The complex carries a net positive change, so it is attracted by the MS pellets, which have net negative charge. Figures 6e and 6f show the resulting morphologies and conceptualised structures at molecular level.

Concluding remarks

The combination of UCS and CBR tests is universally popular and widely used in the design of earthworks. However, due to the limitations of the UCS test for evaluating the stress-strain behaviour of soils and particularly the post-peak response, the results of UCS tests are used here merely as indices for comparing treated and untreated peat samples.

The findings reported in this article indicate that the colloidal NS-MS mixture is effective in enhancing the strength of the peat soil samples tested. The administration of combined nano-silica (NS) and micro-silica (MS) leads to an improvement in unconfined compressive strength by producing a viscous gel, identical to those reported widely in literature (Bahmani *et al.* 2014, Choobasti & Kutanaei 2017, Arora *et al.* 2019, Zhang *et al.* 2019, Ghadr *et al.* 2020b). Incrementing MS content from 6 % to 24 % compromises the compressive strength of peat-NS-MS mixtures. The effect of incrementing MS decreases with setting time. Overall, setting time has clearly beneficial effects. The influence of NS content is heavily dependent on the setting time. In fact, the association of NS content with setting time

follows a peculiar trend that deviates from the earlier observations of Ghadr *et al.* (2020b) in simpler peat-NS systems. At low MS contents, UCS initially decreases with incrementing (from 3 % to 6 %) NS content before partially recovering with a further increase in NS content to 9 %. Greater MS contents change the association between NS and UCS. At 18 % MS content, UCS decreases only marginally with incrementing (from 3 % to 6 %) NS content before sharply increasing with a further increase in NS content to 9 %. At 24 % MS content, UCS is directly associated with NS content. Thus, the effectiveness of NS content is clearly dependent on the MS content. This is indicative of the structure-based behaviour of these multi-modal composites and the significance of mechanisms at the micro-scale.

The findings here differ from previous knowledge of NS-peat composite behaviour. For instance, Changizi & Haddad (2015) and Zhang *et al.* (2019) presented an experimental programme of peat soil stabilisation with colloidal nano-silica in which they showed that higher NS contents almost always compromise the UCS. They also demonstrated the pivotal role of curing time, reporting a direct relationship between UCS and setting time.

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Appendix

Table A1. Physical and chemical properties of Urmia Lake peat (from Ghadr *et al*. 2020b).

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
Bulk unit weight (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 unit weight ($\gamma_{d\,max}$) (kN m^{-3})	12.25
SiO_2 (%)	46.82
Fe_2O_3 (%)	6.08
Al_2O_3 (%)	12.44
Na_2O (%)	0.53
CaO (%)	8.69
MgO (%)	2.78
SO_3 (%)	0.77
K_2O (%)	2.27