Replacing C_3S Cement with PP Fibre and Nanobiosilica in Stabilisation of Organic Clays

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(Received , Revised , Accepted)

Abstract. Organic clays are ideal habitat for flora and fauna. From a geotechnical perspective, organic clays are soft, weak, variable, heterogeneous and flocculated. Portland cement is a universally common stabiliser. However, some organic acids in soil inhibit full hydration and expose cementation products to rapid dissolution. This paper investigates scopes for use of C_3S cement to enable durable cementation. Prospects of using PP fibre alongside with C_3S cement, scopes for partial replacement of C_3S cement with a plant-based nanosilica and evolution of binders are then investigated. Binding mixtures here mimic the natural functions of rhizoliths, amorphous phases, and calcites. Testing sample population include natural and fibre-reinforced clays, compact mixes of clay - C_3S cement, clay - nanobiosilica, and clay, C_3S cement and nanobiosilica. Benefits and constraints of C_3S cement and fibres for retaining the naturally flocculated structure of organic clays are discussed. Nanobiosilica provides an opportunity to cut the C3S content, and to transition of highly compressive organic clays into an engineered, open-structured medium with >0.5 MPa compressive strength across the strains spanning from peak to 1.5-times peak.

Keywords: Clay, peat, organic, improvement, fibre, binder, filler, structure

1. Introduction

Organic clays are compositions of phyllosilicates, nonhumic and humic organic substances. Nonhumic matters are essentially remains of vegetal and animal and comprise cellulose, hemicellulose, sucrose, starch, proteins, amino acids, fats, waxes, resins, and organic acids. Micro-organisms in soil gradually transform the nonhumic matters to polysaccharides and carbohydrates. Decomposition of non-humic matters yield humic matters, that include fatty acids, humic acids, fulvic acids and humins. The ASTM D4427 code of practice classifies soils as organic when the organic content is between 20 and 75 wt.%. This mostly naturally occurring soil is a difficult, unworkable, and intuitively problematic geomaterial with high porosity and compressibility (due to formation of complex metallic, organic, and clayey aggregates see Stevenson 1994), high liquid and plastic limit, high potential of creep, swelling, and shrinkage, very low shear strength that tends to further decrease upon disturbance and exposure to air (Hebib and Farrell 2003; Mitchell and Soga 2005; Saride et al. 2013).

The present study gains stimulus from three directions. Firstly, to study the scopes of using a C_3S cement rather than Portland cement for mechanical stabilisation of organic clays. This first objective is backed by a fraction of literature that shows 'some' organic matters, particularly acetic, humic, tannic, and ethylenediaminetetraacetic acid (EDTA) and sucrose tend to decrease the soil solution pH to low levels, typically between 6.7 and 7.5. At such low pH levels cement hydration products cannot develop, or soon dissolve after development (Tremblay et al., 2002). Organic compounds shield cement constituting crystals, consume the Ca^{2+} needed for their hydration, and consequently inhibit cementation. Secondly, to determine whether small contents of fibre can mitigate the inherent brittleness of C_3S cement-stabilized clays. Thirdly, to study scopes for partial to total replacement of C_3S cement with a plant-based alternative that mimics the natural functions of rhizoliths rootlets, and silicious amorphous phases.

1.1 Environmental effects of engineering peat

Wetlands are home to peat and over 40% of the carbon stored in soil is that locked in peat. From the total 1220 registered wetlands in the 1975 Ramsar Convention, 25 belong to Iran, draping an area of 1,488,781 ha size — that is about 0.85% of the Iranian landmass. Largest Iranian Wetlands is the Lake Urmia (i.e., the study site) of 483,000 ha area. It is encompassed by vast brackish marshlands. As of any other wetland, the peat in Urmia Wetland is a natural carbon store. Peat can store carbon as long as it remains wet but dewatering and drainage of peat prior to construction can cause the groundwater level to drop, exposing the peat to air and creating an oxic peat layer. This layer promotes aerobic decomposition, releasing carbon as CO_2 into the atmosphere and contributing to the greenhouse effect. The

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release of carbon into the atmosphere threatens the role of wetlands and organic matter in controlling global carbon emissions. To this end, engineering peat, although inevitable, will have environmental ramifications. An objective of this paper is to work towards limiting the extent of damage to peat due to engineering interventions.

1.2 A local solution to a global challenge

Urmia Lake (about 1273 m above sea level) is a hypersaline shallow lake with about 5000 km^2 of surface area and about 52,700 km^2 basin area (Kelts and Shahrabi, 1986). It holds about 32 billion cubic meters of water with an extremely high 140-280 g.L^{-1} salinity. The lake is one of the sixth largest salt lakes on earth. Designated as a biosphere reserve in the 1971 Ramsar Convention and a National Park in 1975, the lake is an ecologically sensitive area and home to over 100 islands and over 830 living species (Scott 1995) including Artemia Urmiana brine shrimp, flamingos and pelicans, Iranian yellow deer, egrets, and ducks (Schulz et al. 2020).

A lake crossing was constructed in 2008, constituting 8.5 miles of approach earthworks and 1.1 mile of bridge. Much of the earthworks were conducted into and on sequences of alluvium, soft clay, peat, and a layer of up to 12 m thick organic clay. Disturbance of peat led to a prolonged course of creep settlements, the effects of which continue to be felt today. Similar creep settlements are reported in McDonald and Cimino (1984) and Tashiro et al. (2015), inter alia, for the West Gate Freeway built on the slightly organic Coode Island silty clay and Maizuru–Wakasa expressway, respectively. The theoretical backgrounds of creep settlement of organic soils are discussed in Olson (1998) and Huat et al. (2019). Cement stabilisation is widely adopted to mitigate that compressibility (Kalantari et al. 2010; Kalantari 2011; Lemos et al. 2020; Paul and Hussain 2020).

Stabilisation of organic soils with Portland cement however is proved not necessarily effective, or as effective as one would hope so. Some organic compounds, particularly humic and fulvic acids, interact with calcium and aluminum, decrease the pH of soil solution, and inhibit the cementation. In this, some acids consume cations needed for formation of hydrated calcium aluminate or C-S-H units (Harris et al. 2009; Pan et al. 2019). The debatable effectiveness of calcium-based binders for improvement of soft organic clays led to an interest in utilization of alternative binders, including bio-cements (Latifi et al. 2016) and biomass silica stabilizers (Hassan et al. 2019). To this end, a range of alternative stabilizers have been trialed and reported in literature. These include fly ash (50 wt.% of total binding material) in Axelsson et al. (2002); fly ash and lime (43 wt.% of total binding material) in Hebib and Farrell (2003), and micro-silica in Kalantari et al. (2011) and Ghadr et al. (2020). There have been some attempts in using site-won soils as a component of binder (e.g., Jorat et al. 2013; Kalantari and Rezazadeh 2015). Use of combined fillers and binders in form of grouts has received some interest (Berti et al. 2021). The simplest and most common filler is sand. For example, Kolay and Aminur (2011) reported on successful administration of a grout that constitute sand of 50 wt.%. Other filler types include sodium bentonite (Wong et al. 2013), and shredded tire (Rahgozar and Saberian 2016). Methods share a common concept: to fill void spaces with an impermeable binder and transform the organic medium into a cemented hard base. In Assadi-Langroudi et al. 2022, we set out needs to move away from densification to nature-inspired ways of ground engineering; to retain soils' natural ecological service provisions whilst making them fit for engineering needs. This study follows this ideal and investigates scopes for Stabilising organic clays in their naturally open microstructure.

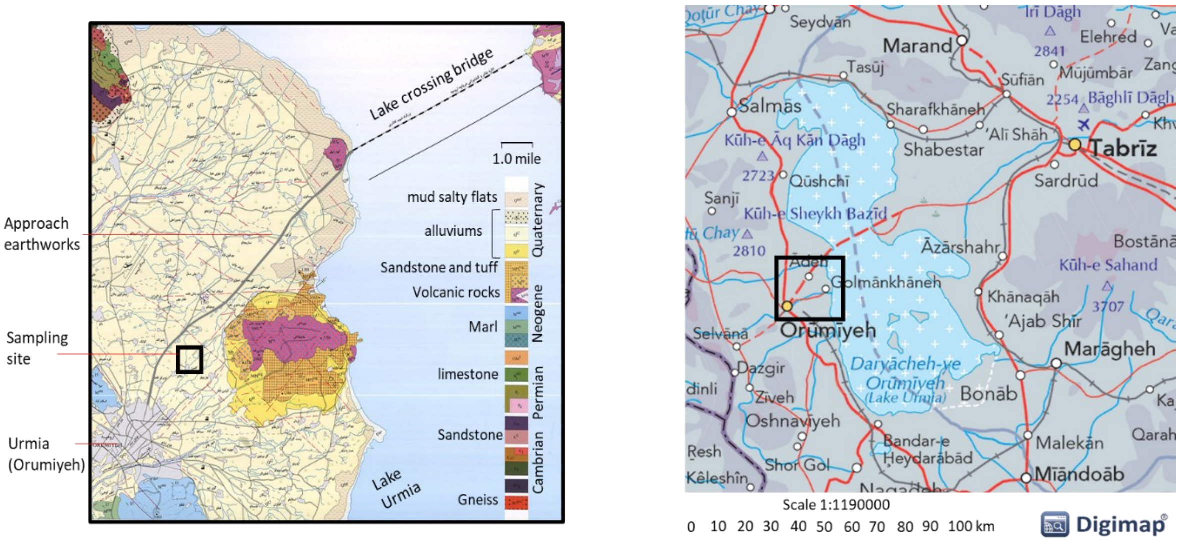
2. Materials and Methods

The testing programme described here is designed to study scopes for using a nanobiosilica substance as an alternative for C_3S cement for engineering of highly organic clays. It is established that randomly distributed fibres can add a degree of tensile strength and relax desiccation cracking during dry spells. The added tensile strength may also compensate for the compromised hydration incurred by effects of organic matters. To this end, effects of fibre in clays mixed with varied contents of C_3S cement and nanobiosilica are also studied. Unconfined Compressive Strength (UCS) is adopted to quantify the stress-strain behaviour of 27 conditioned soils. Samples include natural and fibre-reinforced clay, compact mixes of clay - C_3S cement, clay - nanobiosilica, and clay, C_3S cement and nanobiosilica. Curing time and fibre inclusions are varied across sample population.

2.1 Materials

2.1.1 Base soil and habitats

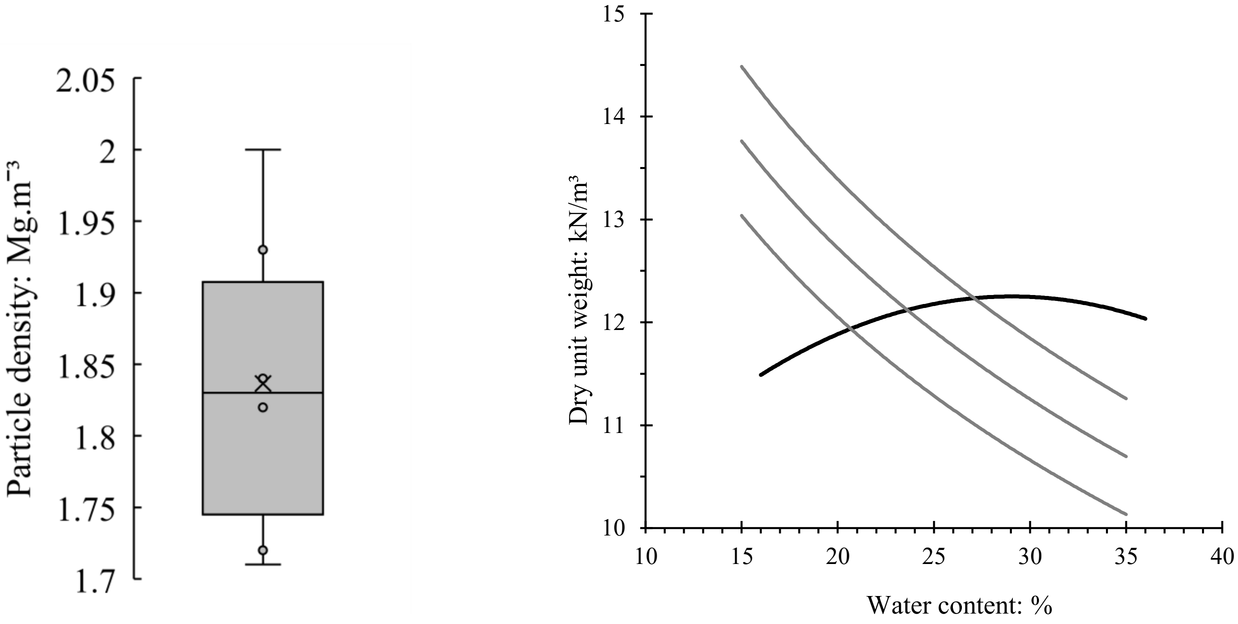
Six samples of organic alluvial clay were obtained from the shoulders of Urmia-Tabriz Highway, 10 miles southwest of Lake Urmia crossing bridge, near the Golmarz Wetland (Fig. 1 – 37.602231, 45.121081). Samples were obtained from 0.3 and 0.7 m depths. Water level at the time of sampling was below the bed of excavated trenches. The obtained clays were soft, marshy, dark brown in colour and contained rootlets from surficial plant species. Common plant species across the region and around sampling site include Plantago lanceolata and Centaurea solstitialis. The latter is a rich source of tannic acid, corresponding with the relatively low pH of soil solution in Table 1. The wetland habitat types in the region includes Chenopodioideae and Amaranthaceae, Poaceae, Cyperaceae. Within the excavated profile, the degree of decomposition clearly increased with depth. The main physical characteristics of material are summarized in Table 1 and Fig. 2. The clay is classified as CE (clay with extremely high plasticity). In von Post (1992) scale, the clay falls under the vPH humification H10 class. In this, organic compound of the material is completely converted and decomposed (in von Post scale) and contains insignificant organic fibres. Fig. 3 presents the chemical characteristics of base soil.



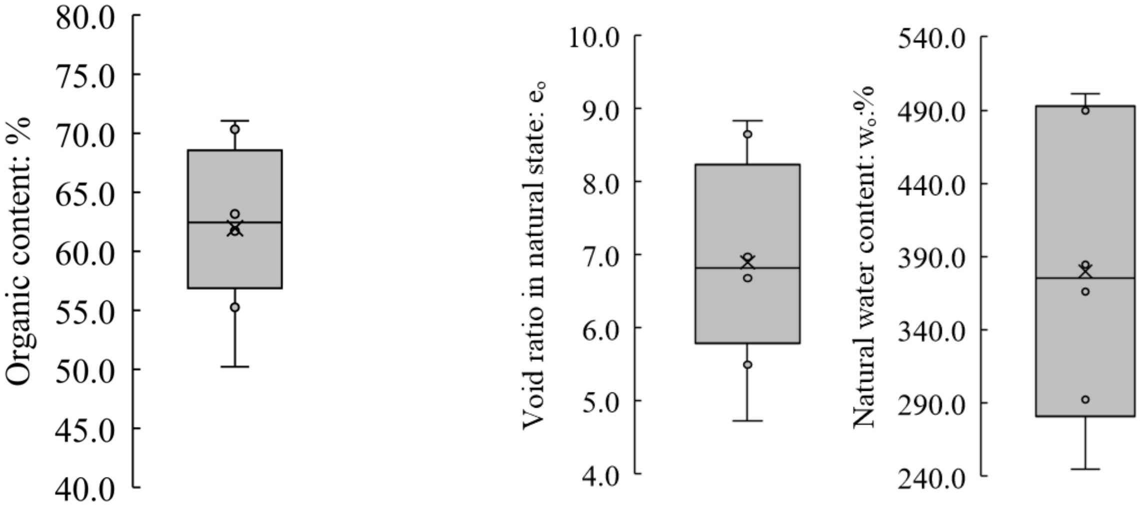
(a) Geological map (b) Ordnance Survey map

(c) Landscape around the sampling site (d) Sampling dig

Fig. 1 Location of sampling



(a) Density (b) Dry unit weight

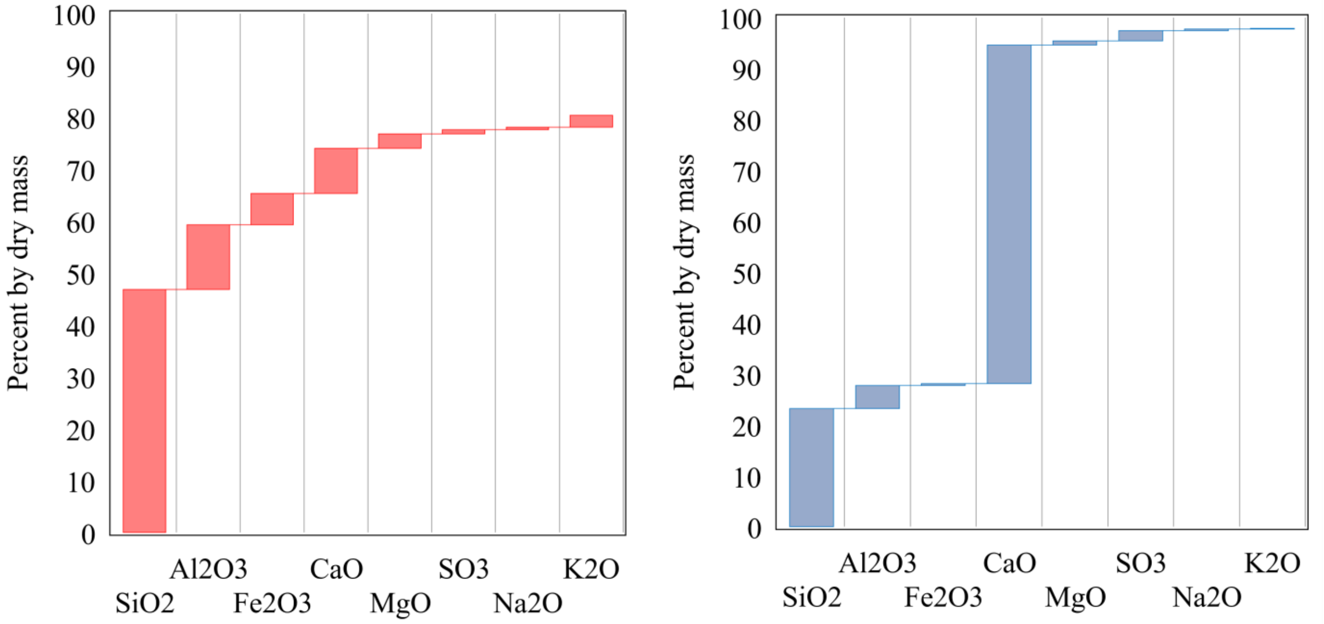


(c) Organic content (d) Void ratio water content in natural state and

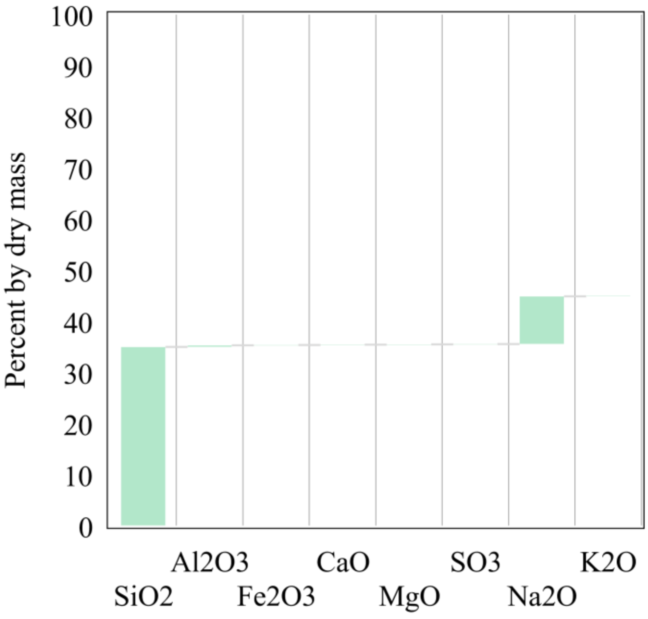
Fig. 2 Physical properties of collected organic clay samples

2.1.2 Other materials

For a subset of test specimens, a fraction of base soil was mixed with C_3S (locally known as Pozollana) cement. The cement was supplied, in-kind, by the Urmia White Cement Company located 9 miles from the sampling site (37.75193, 45.04476). The cement is rich in calcium oxide (66.5 wt.% in Fig. 3 that is the upper end of 60-67 wt.% for Ordinary Portland Cement, OPC), low in aluminum oxide (5.53 wt.% in Fig. 3 that is the lower end of 3-8 wt.% for OPC), and deficient in ferric oxide (0.4 wt.% in Fig. 3 that is lower that 0.5-6 wt.% bracket for OPC). It has a low hydration temperature, a high 2.87 CaO/SiO_2 ratio, and nearly 58% tricalcium silicate C_3S clinker — that is 8% higher than 50% C_3S for rapid hardening cements. These properties combined can potentially compensate for the calcium cations consumed by soil organic matters. Sulphate content is low, making the cement a generally basic material. The 28-day compressive strength of cubic blocks for testing cement is 67 MPa and the Blaine grade is 4200 ± 200 $cm^2.g^{-1}$. Table 1 and Fig. 3 summarise the chemical properties of C_3S cement. Thermoplastic polymeric micro-synthetic fibres of 19 µm in diameter (D_f), 12 mm in length (l_f), and 170 MPa tensile resistance were used as fibrous matter in a subset of test specimens. These are commonly used as reinforcement in concrete and are commercially available. A nature-based nanobiosilica from calcination of rice bran (i.e., harder outer layer of cereal grain) was provided in-kind by the Agricultural Engineering Research Institute in a 30% colloidal form. This is an amorphous silica from agricultural waste that otherwise is gathered in open heaps near mills and burnt by farmers. Rice bran from farm mills were washed, screened and calcinated at 700˚C. Incinerated ash was then treated with ethanoic acid (i.e., vinegar acid) and centrifuged at 2,500 rounds per minute rate. The extract is further treated with sodium hydroxide, acid sulfuric, ammonium hydroxide and hydrochloric acid. Table 1 and Fig. 3 summarise the chemical properties of nanobiosilica. The product has an average particle size of 15 to 20 µm, a particle density of 1.2 Mg.m^{-3}, a pH of 9.0 to 10.5 (ASTM D:4972-95a) and a viscosity of 5.5 cP.



(a) Base clay (b) C$_3$S cement



	Clay 🟥	C_3S cement 🟦	Nanobiosilica 🟩
SiO_2	46.82	23.18	34.98
Al_2O_3	12.44	4.53	0.27
Fe_2O_3	6.08	0.39	0.07
CaO	8.69	66.5	0.07
MgO	2.78	0.77	0.05
SO_3	0.77	2.01	0.097
Na_2O	0.53	0.35	9.30
K_2O	2.27	0.12	0.12

(c) Dried nanobiosilica (d) Contents in percent

Fig. 2 Chemical compounds by X-ray fluorescence

Table 1 Properties of the sample

Property	Procedure	Values
Base clay soil		
Natural moisture content: %	ASTM D2216 - 19	240-500
In situ bulk unit weight: kN/m^3	ASTM D7263 - 21	10.2-11.8
Specific gravity	ASTM D854 - 14	1.84
Liquid limit: %	ASTM D4318 - 17e1	153.3
Plastic limit: %	ASTM D4318 - 17e1	82.5
Organic content: %	ASTM 2974	60.6
Optimum moisture content: %	ASTM D698 - 12	29.0
Maximum dry unit weight: kN/m^3	ASTM D698 - 12	12.25
Initial void ratio	Phase relationships	4.7-8.8
pH (of soil solution)	ASTM D4972 - 95a	6.8-7.6
SO_4: ppm	Ion chromatography	480-660
C_3S cement		
Loss on ignition: %	ASTM D7348-21	3.39
Tricalcium silicate, C_3S: %	X-ray powder diffraction	57.70
Dicalcium silicate, C_2S: %	X-ray powder diffraction	22.89
Tricalcium aluminate, C_3A: %	X-ray powder diffraction	11.34
Tetracalcium alumioferrite, C_4AF: %	X-ray powder diffraction	1.19
Nanobiosilica (hydrosol)		
Loss on ignition: %	ASTM D7348-21	55.00
O^{2-}: wt. %	Atomic absorption spectroscopy	59.89
Si^{4+-}: wt. %	Atomic absorption spectroscopy	33.96
Na^{+}: wt. %	Atomic absorption spectroscopy	3.67
Al^{2+}: wt. %	Atomic absorption spectroscopy	0.87

2.2 Sample Preparation

One sample preparation strategy was designed and delivered for the entire sample population. Obtained base clays from site were air-dried for 7-10 days. Clods were crumbled with a rubber pestle, pulverized, and passed through a sieve with mesh sized 300μm. Materials remaining on sieve were crumbled and screened again. The pulverized soil was thoroughly mixed to ensure a reasonable degree of homogeneity. These were placed in sealed buckets and stored in a dry, dark, cool area of laboratory. Static compression was used to construct test specimens. Water content was first increased to 29%. Deionised water was used throughout. Where cement was intended as binder, C_3S cement powder was added to wet soil at pre-determined dry equivalent mass (see Table 2) and mixed with the wet base soil. For mixtures containing PP fibres and to prevent floating, fibre was added to soil in small, equal, and controlled amounts ahead of wetting. Fibre content was kept constant at 0.5 wt.% for all specimens — this is consistent with many previous studies on soft clays (e.g., Fatahi et al. 2012; Yadav and Tiwari 2016). For mixtures containing nanobiosilica, the mass of water within the colloidal solution was considered in determining mass of total added water. Wet soil mixtures were then thoroughly mixed using a miniature electric mixer. Mixed soils were kept in sealed containers for 10 hours to mellow (overnight). Wet compositions were then compressed into standard Unconfined Compressive Strength UCS split moulds, 38 mm in diameter and 80 mm in height. The specimens were then cured (aged) for 7 and 28 days. These were wrapped in cling film and stored in sealed containers in an environmental chamber at a constant 20 ± 3°C temperature.

2.3 Testing Methods

After 7 and 28 days of curing, specimens were subjected to UCS test using a universal loading frame measurement to measure the stress-strain behaviour. Tests were carried out at a constant strain rate of 1 mm.min^{-1} and in accordance

Table 2 Specimen and test diet

Compositions	C_3S cement: %	Nanobiosilica: %	PP fibre: %	Curing: days
Clay	0	0	0	0
Clay+ Fiber	0	0	0.5	0
Clay+ Cement	4,6,8,10	0	0	7,28
Clay+ Cement+ Fiber	4,6,8,10	0	0.5	7,28
Clay+ Nanobiosilica	0	5,10,15,20	0	7,28
Clay+ Nanobiosilica + Fiber	0	5,10,15,20	0.5	7,28
Clay+ Cement+ Nanobiosilica + Fiber	4	5	0,0.5	7,28
Clay+ Cement+ Nanobiosilica + Fiber	6	10	0,0.5	7,28
Clay+ Cement+ Nanobiosilica + Fiber	8	15	0,0.5	7,28
Clay+ Cement+ Nanobiosilica + Fiber	10	20	0,0.5	7,28

with methods in ASTM D2166M-16. Tests were repeated twice for each composition. Scanning Electron Microscopy (SEM) observation of soil microfabric was conducted on a subset of specimens following the UCS experiments. Specimens were dehydrated slowly through air-drying. Small, 5 to 7 mm in width cubic sub-specimens were extracted from the middle of UCS specimens. The undisturbed face chosen for microscopy aligned with the vertical axis of UCS specimens, perpendicular to the bedding. To remove the hygroscopic moisture, sub-specimens were put under 10-4 kPa vacuum pressure and coated with four thin layers of carbon using an Agar auto carbon coater. Low vacuum SEM was adopted to suit the non-conductive nature of organic matters with high water retention capacity.

3. Results

3.1 Cementation in micromorphological context

Fig. 4 presents particle-level SEM snapshots of four main binding matters synthesised through this research. The scale bar measures 1µm for all micrographs for comparability reasons. Fig. 4a presents the flocculated structure of C-S-H units in a micrograph of clay mixed with 8 wt.% C_3S cement. Mixing the base clay with cement leads to formation of lime, and calcium-silicate-hydrate (C-S-H) upon hydration of alite phase (C_3S) see Eq. (1), and belite phase (C_2S) see Eq. (2). The C-S-H is the main cement hydration product and occupies 50 to 65% by volume of cement paste. The C-S-H forms a flocculated, trellis-like structure in SEM micrographs. The C_3A phase alongside with the CSH2 (gypsum) hydrates to form ettringite Eq. (3). The abundance of sulphates in base soil (480-660 ppm in Table 1) guarantees the stability of ettringite. Transition of the latter into monosulfate aluminate hydrate crystals of reasonable stability requires sulphate deficiency. The relatively low pH of base soil solution corresponds well with the high sulphate content. Ettringite minerals appear in form of short, thin stick-like units in SEM micrographs (see Fig. 4b).

$$Ca_3SiO_5 + 5.2H_2O \rightarrow (CaO)_{1.8}.SiO_2.(H_2O)_{4.0} + 1.2Ca(OH)_2 \quad (1)$$

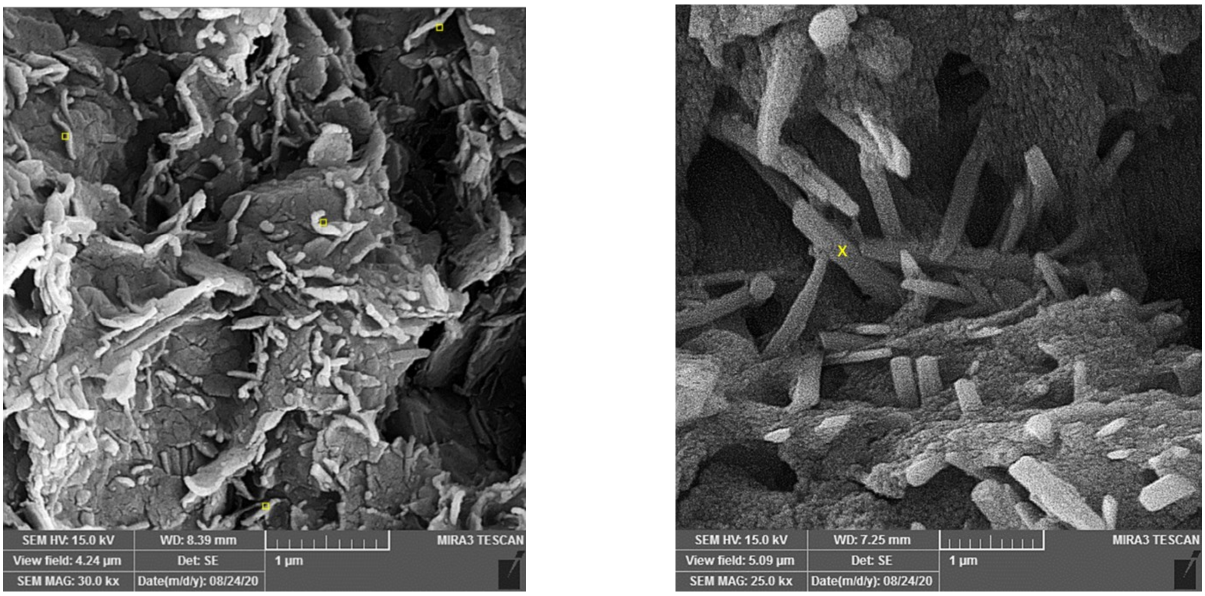
$$2Ca_2SiO_4 + 4H_2O \rightarrow (CaO)_{3.0}.(SiO_2)_2.(H_2O)_{3.0} + Ca(OH)_2 \quad (2)$$

$$Ca_3Al_2O_6 + 3CaSO_4 + 32H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O \quad (3)$$

On administration of colloidal nanobiosilica to soil, crystals of silica begin to form on the surface and contact points of clay platelets. Fig. 4c illustrates precisely defined silica crystals with bright fuzzy surface. Silica blocks lend friction to otherwise smooth clayey bedding planes. With increasing curing time and nbS content, silica crystals accumulate to form larger flocs. These are smooth units of platy shape that extend to onionskin shields around particles (Fig. 9a).

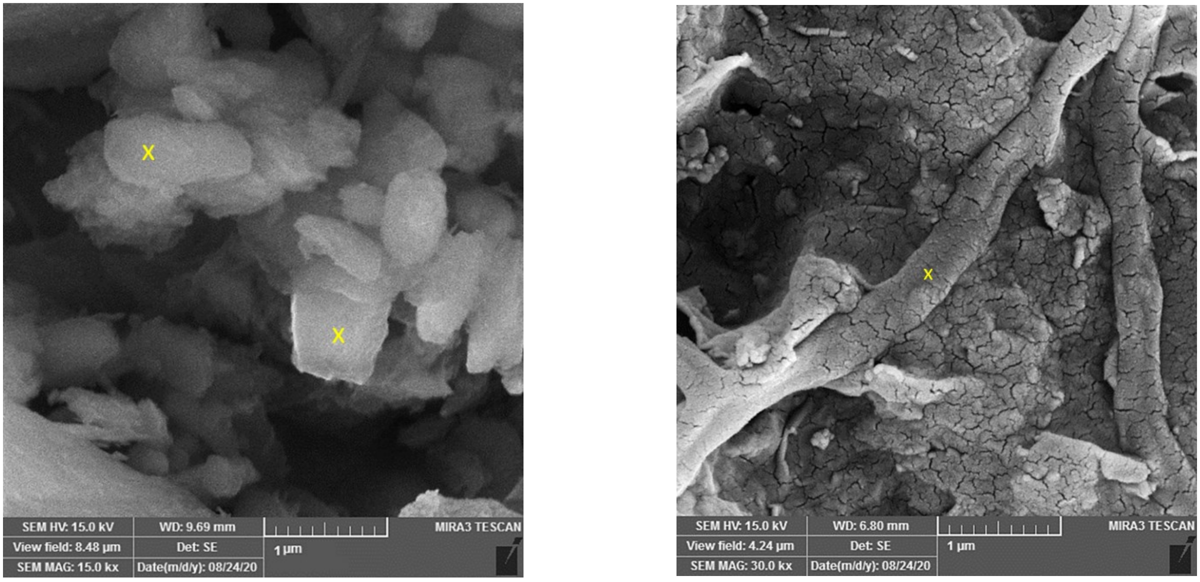
In Eq. (2), calcium hydroxide (hydrate) precipitate to form meshwork of threadlike needles, diffusing around rigid bodies. These are much finer than fibres, finer than ettringite, and much shorter than aragonites. Through the next sections, SEM micorgraphs containing clods of calcium hydroxides will be presented. These are rare, and once occurring, rest on sides of rigid particle assemblages, within the pore space.

Micro-synthetic fibres (D=19 µm, l=12 mm) twine aggregates together and mobilise their inherent tensile capacity to improve the overall residual strength. Fig. 4d illustrates a SEM micrograph of multiple intertwined aggregates with synthetic fibres. It will be shown that disturbance of cemented matrix (i.e., C-S-H, nanobiosilica shields) is a potential drawback of fibres, with possible negative implications on peak strength.



(a) Ettringite and lamellar C-S-H structures

(b) Ettringite ‘sticks’ encrusting some void spaces



(c) Homogeneous nucleation of nanobiosilica

(d) PP fibres and flocs of calcium hydroxide

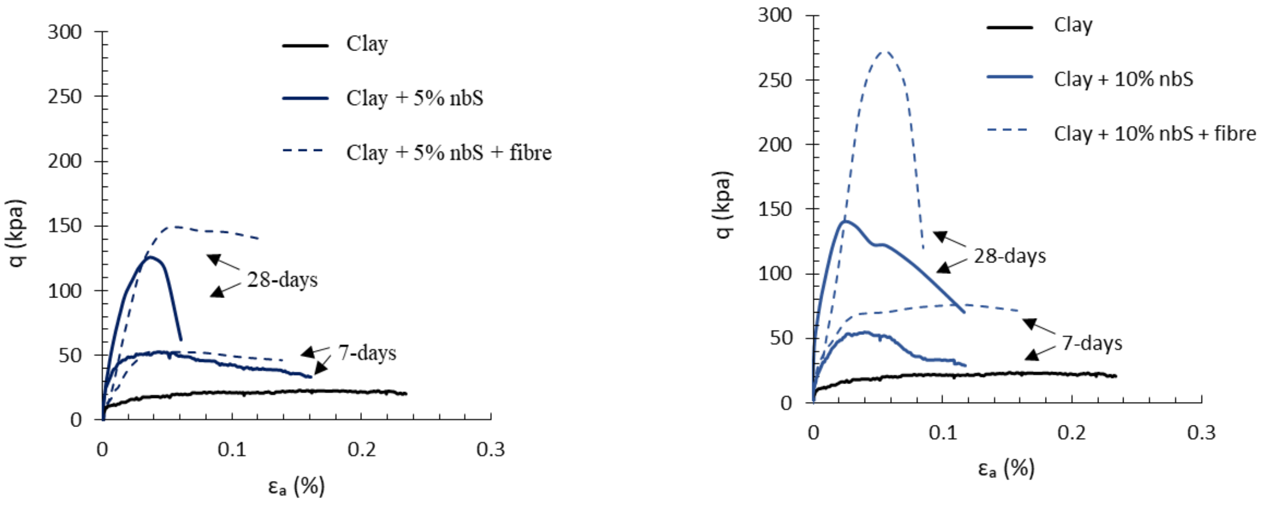
Fig. 4 Main micromorphological forms appearing in various stabilised clays in this research

3.2 C_3S as an alternative cement

The axial unconfined compressive stress is plotted against axial strain in Fig. 5, for base and cement-stabilised clay specimens, with and without fibre inclusions and for two levels of curing. Immediate inspection confirms the effectiveness of C_3S cement as an effective stabilizer for testing organic clay. The gain in compressive strength becomes more prominent for greater cement contents. The stress at peak increases by 200% to 2,400% for clays stabilized with 4 to 10 wt.% C_3S cement. The gain in strength picks momentum with ageing. After 28 days, the stress at peak increases by 1,000% to 4,200% upon stabilization with 4 to 10 wt.% cement.

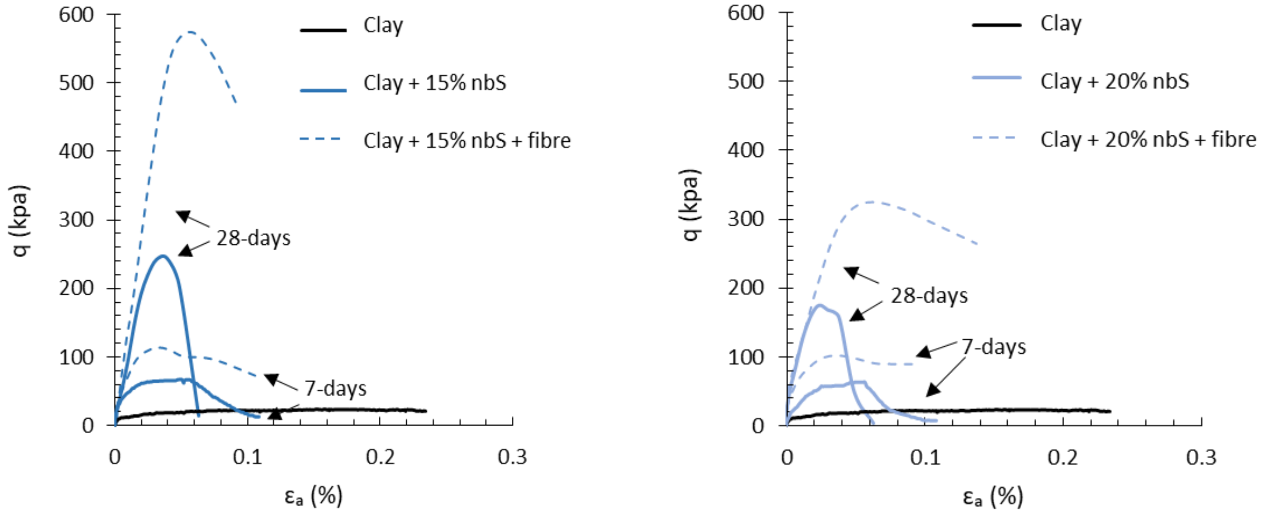
For specimens containing ≤6 wt.% cement, residual strength (at an applied strain of 1.5 times peak strain) increases with cement content, in the first 7 days post treatment. This is welcomed but is followed by a rapid loss of residual strength as specimens age further. For specimens containing >6 wt.% cement, residual strength decreases with both cement content and curing time. The difference between peak and residual strength is indicative of brittleness. To this end, the sudden loss of strength appears to be generally a concern with cement-stabilized specimens and clearly linked to cement hydration. It will be shown in the discussion of results that collapse of void spaces encrusted with ettringite is a likely cause.

To relax this troublesome brittleness, specimens were mixed with 0.5 wt.% of PP fibres. In Fig. 8b, reinforcement of base clay with fibre provides an almost 100% rise in compressive strength, an explicit improvement to the modulus of elasticity, and a clear strain hardening behaviour. For cement-stabilised specimens, fibre slightly compromises the compressive strength (see for example stress-strain curves for 8 and 10 wt.% cement content). It however relaxes the brittleness, enabling greater levels of



(a) Clay, 5% nbS, (0-0.5%) fibre

(b) Clay, 10% nbS, (0-0.5%) fibre



(c) Clay, 15% nbS, (0-0.5%) fibre

(d) Clay, 20% nbS, (0-0.5%) fibre

Fig. 6 Variation of axial stress with strain

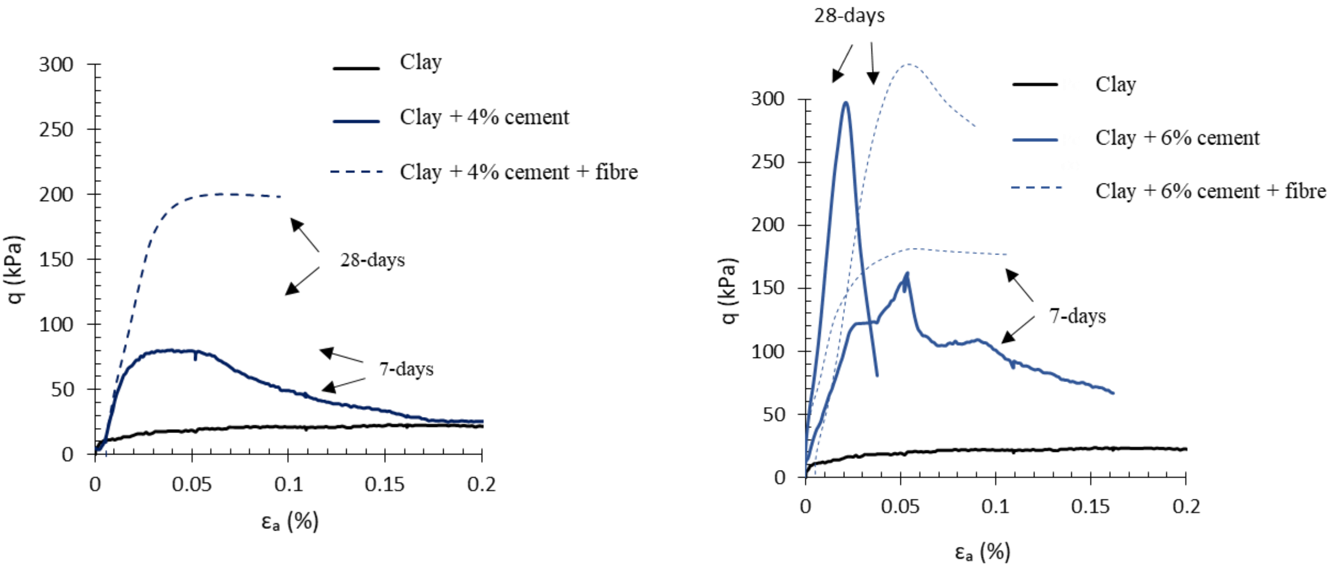
stress at strains above peak strain.

3.3 Nanobiosilica as an alternative binder

In Fig. 6, the administration of nanobiosilica (nbS) to clay improves the compressive strength of testing organic clay. The gain in strength is modest when compared with levels seen upon C_3S cement stabilization. In the short-term, the stress at peak marginally increases with nbS content between 5 to 15 wt.%. Further increase in nbS content from 15 to 20 wt.% leads to partial loss of strength. The 28-day specimens follow the same trend; however, the gain and loss in strength becomes sharper. This is a curious observation. Unlike cement, nbS does not set via hydration.

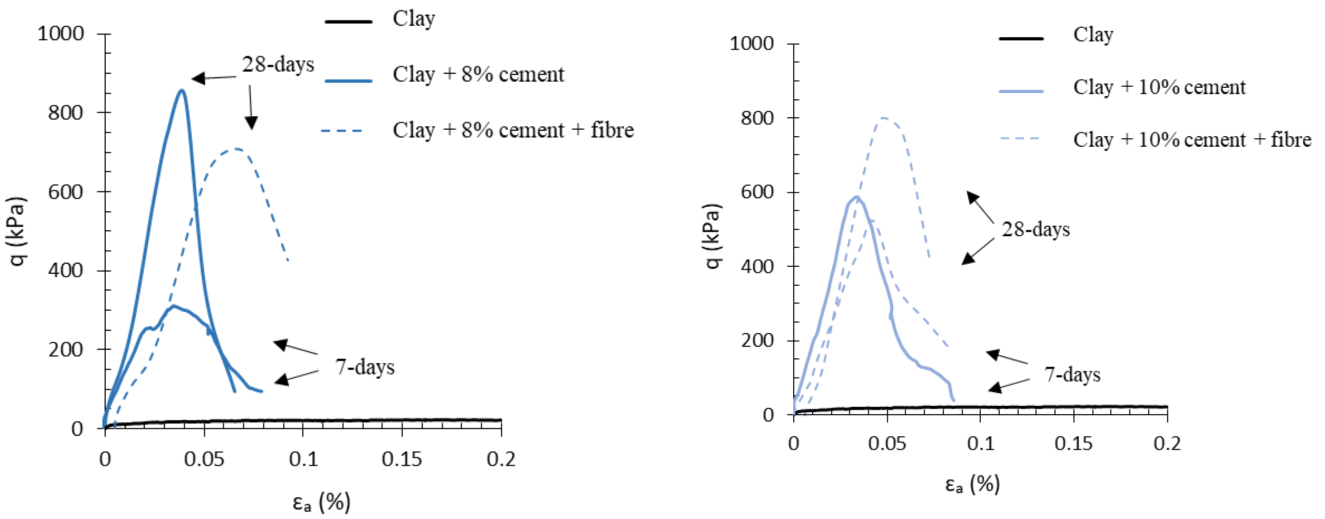
In the discussion of results, interactions between sulphate in organic matters and silica will be brought as an explanation for sharp rise (and fall) in strength with time. The gelation of flocs on base soil's surface and resulting interlocking will be offered as an explanation for direct correlation between nbS content and strength. It will be shown that, an increase in nbS content from 15 to 20 wt.% marks emergence of silica shields and progressive disappearance of silica flocs.

An exciting feature on Fig. 6d is the continuous increase in strength with nbS content across the full strain range, for 28-day specimens. This shows the significance of polymineral coating units that result from long-term interaction between sulphates and silica. Contribution of fibre to compressive strength of nbS-mediated soils is remarkable. The gain in strength is substantial across the full strain range. For 28-day specimens and similar to high 8-10 wt.% C_3S mixtures, addition of fibres to high 20 wt.% nbS decreases the strength to levels lower than 15 wt.% nbS. In discussion of results, this will be attributed to disturbance of otherwise homogeneous polymineral sulphate-silica shields.



(a) Clay, 4% cement, (0-0.5%) fibre

(b) Clay, 6% cement, (0-0.5%) fibre



(c) Clay, 8% cement, (0-0.5%) fibre

(d) Clay, 10% cement, (0-0.5%) fibre

Fig. 5 Variation of axial stress with strain

3.3 Interim key findings, objectives, and pathway

To this end, C_3S cement and nanobiosilica hydrosol are proved effective in improving the compressive strength of testing organic clay. Improvement mechanisms vary. The C_3S mixtures gain strength via hydration and precipitation of three new products: C-S-H, ettringite and calcium hydroxide. Ettringites exhibit dual functions. They line and protect a proportion of soil pore networks and in this, provide conduits for air and water, hence ecological benefits. Pore networks however are susceptible to collapse upon excessive straining and generate an unwelcomed quality of brittleness. Fibres mediate the brittleness at the cost of overall limited gain in strength. Nanobiosilica (nbS) flocs instate a quality of interlocking among clay platelets and organic substances. At greater concentrations, flocs adopt a laminar shape, forming buttress units and coatings. These arrest the strains and enhance the strength (see Discussion). High concentration of SO_4^{2-} in soil solution alters the nbS into complex polymineral coating units (see Discussion) and provide additional strength with ageing. The effectiveness of these polymineral units become remarkable as specimens age. In the short-term, combining the nbS with fibres doubles the strength at peak and residual state. In the long-term, mixing fibre with nbS triples the strength at peak and residual state. The 7-day compressive strength of 10 wt.% C_3S-0.5 wt.% fibre mixtures is only slightly lower that the 7-day compressive strength of 15 wt.% nbS-0.5 wt.% fibre, indicating the dominant control of fibres on overall stress-strain behaviour, hence their significance. Fibres however are ‘disruptive’ as they thread through laminar forms of binders — these count for C_3S at almost any content and nbS at >15 wt.%.

In design of a new composite binder, three principal objectives are followed. An ideal binder should,

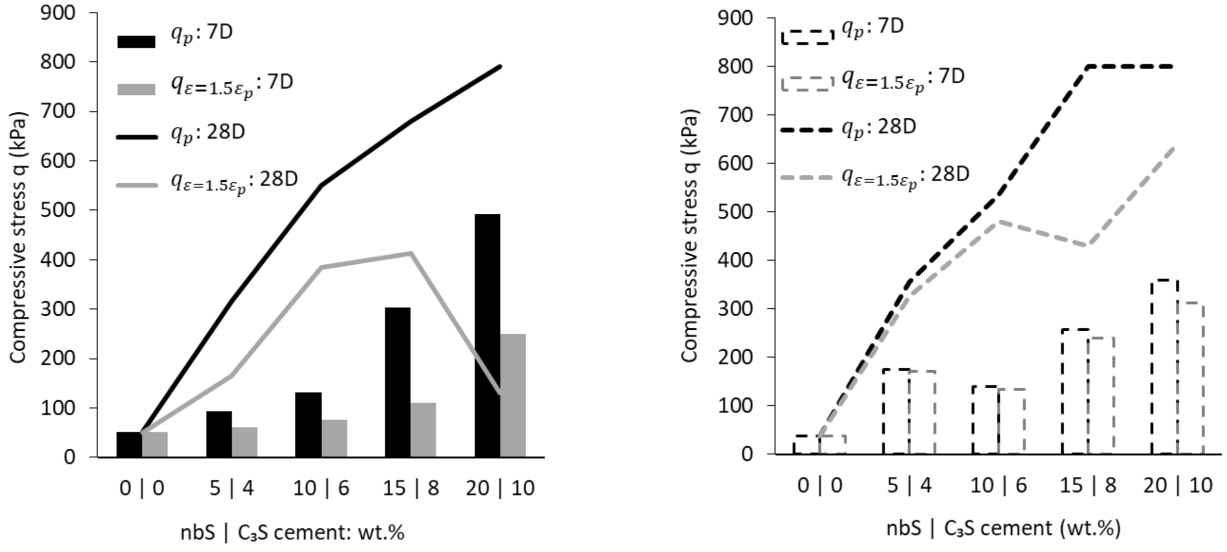
i. includes minimal C_3S content to provide: at least

0.5 MPa compressive peak and residual strength; and, open, braced network of pore spaces that service ecological functions of peat;

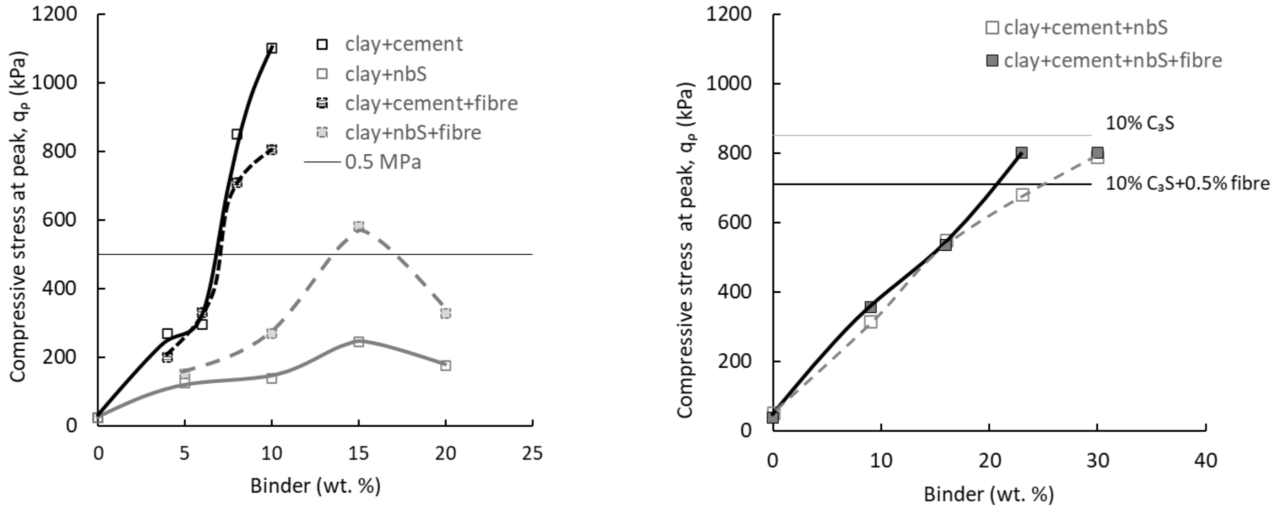
ii. include minimal fibre content to provide: stability to retained pores at large strains; and, create new phase of protected pore spaces;

iii. include nanobiosilica to provide: little to no brittle plastic behaviour; and, an additional source of organic matters

Four mixtures of cement and nanobiosilica are synthesised and administrated to the testing organic clay. The total binder content ranges from 9 to 30 wt.%. Detailed account of preparation methods is given in earlier sections.



(a) Clay, 5-20% nbS, 4-10% C_3S (b) Clay, 5-20% nbS, 4-10% C_3S, 0.5% fibre

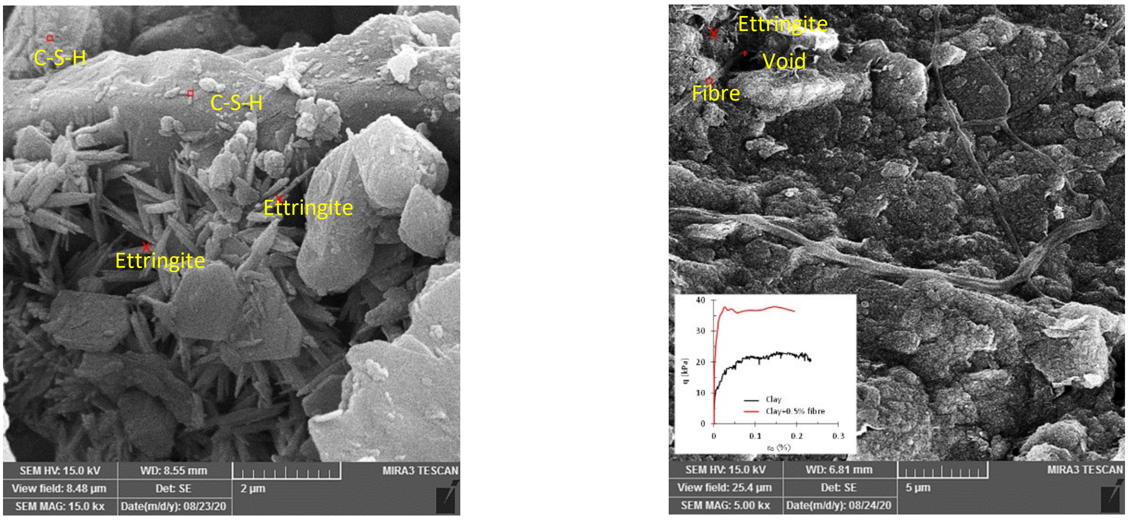


(c) In one frame, effectiveness of C_3S and nbS as single binder (d) In one frame, effectiveness of C_3S-nbS mix as compared against C_3S as single binder

Fig. 7 Variation of axial stress at peak strain, and 1.5-times peak strain

3.4 Interim key findings, objectives, and pathway

Fig. 7a demonstrates the variation with binder content of stress at peak and residual strains. The rapid build-up of strength with binder content and the gap between 7-day and 28-day envelopes are indicative of C_3S hydration as a major factor. The rate at which soil gains strength however diminishes with binder content. This is visible in Fig. 7a (for 28-day specimens) and much more explicit in Fig. 7b (again, for 28-day specimens). A micromorphological change will be offered as explanation in the 'Discussion' section. In Fig. 7a, brittleness is manifested by the gap between envelopes representing stress at peak and 1.5 times peak strain. The nbS component of C_3S-nbS mix is clearly not an effective remediation for brittleness. Fibre inclusions however do relax the brittleness. This is manifested in the narrower gap between envelopes representing stress at peak and 1.5 times peak strain in Fig. 7b (as opposed to Fig. 7a). To this end, the nbS-C3S mix can satisfy the three criteria brought in the previous section: both peak and residual strength can reach ≥0.5 MPa. Fibre can be used to almost eradicate brittleness, and hence the collapse of open pore spaces. Nanobiosilica can relax the use of C_3S cement and offer similar services for improvement of



(a) Without fibre

(b) With fibre — also, axial stress strain behaviour of testing organic clay in original form and in mixture with 0.5 wt.% fibre

Fig. 8 SEM micrographs of cement-stabilised clays

peculiar, highly organic clays

In Fig. 5d, adding 10 wt.% C_3S and 0.5 wt.% fibre to the base soil yields a peak and residual strength of 800 and 430 kPa in order. This is the most ideal condition that one can expect from the testing improved organic clay, i.e., a UCS>0.5 MPa across the spectra of strains. In Fig. 7b and Fig. 7d, base soils mixed with a slightly lower 8 wt.% C_3S and 0.5 wt.%, with pore water containing colloidal nanobiosilica (providing 15 wt.% nbS solids) yield an exact similar peak and residual strength. This is an important finding. A carefully adjusted C_3S content can be relaxed through partial replacement with nbS that is known to offer far less levels of strength. The diagrams in Fig. 7 can be of practicing engineers' interest in designing binders bespoke to specific bearing capacities.

4. Discussion

4.1 Hydration, potential reversal, and mitigation

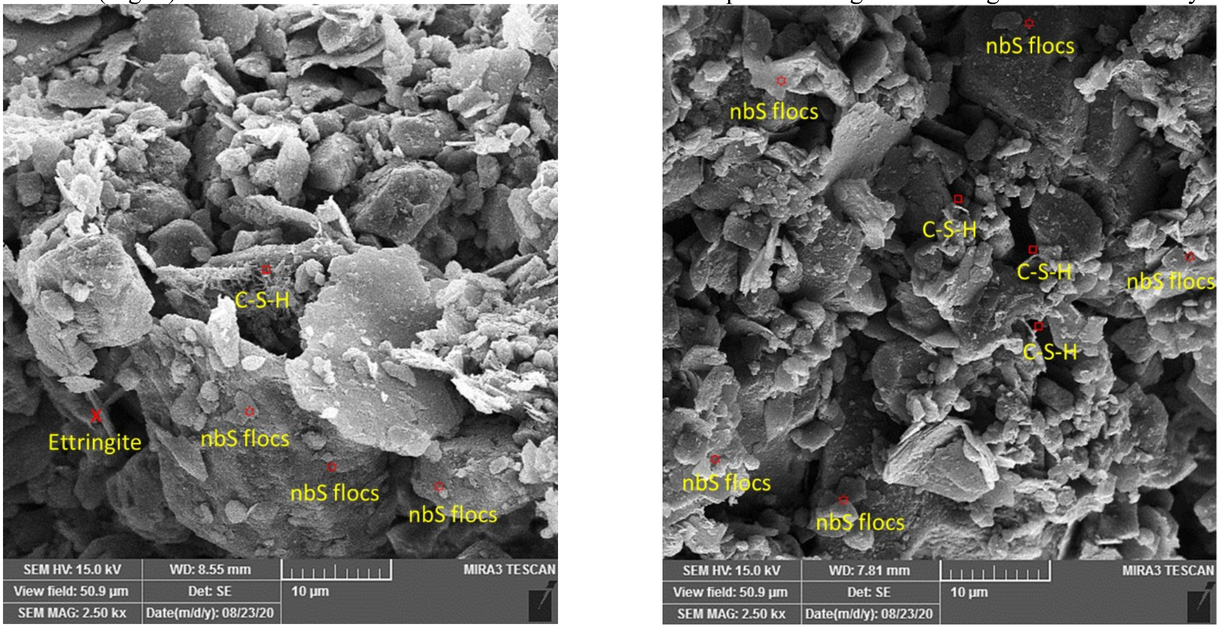
In Eqs (1)-(2), calcium hydroxide is presented as a hydration product. Within the pore fluid, calcium hydroxide appears in colloidal form and acts as Ca^{2+}-rich electrolyte. When exposed to such electrolyte, clay donates one hydrogen atom (i.e., proton) from its hydroxyl tail. The phenomenon is generally referred to as deprotonation (Van Olphen 1977). The oxygen atom at deprotonated hydroxyl tail attracts Ca^{2+} (.Ca.) followed by a free hydroxyl (:Ö̤.H). Interplay between clay and calcium hydroxide were initially discussed by Taylor (1961) and then Herzog and Mitchell (1963). They referred to a decrease in the lime concentration within the pore fluid phase which is balanced with extraction of lime from other hydration products, particularly the C-S-H. The consequent damage to C-S-H is unlikely here. The use of C_3S cement and hence provision of Ca^{2+} above typical levels in ordinary Portland cement appears to have protected the C-S-H structure against loss of lime. This is evident in Fig. 5 and direct correlation between C_3S cement and stress at peak.

4.2 Brittleness and mitigation

The abundance of ettringite (Fig. 4b) thanks to high concentration of SO_4^{2-} in soil solution containing tannic acids is one cause of gain in peak strength with cement-stabilised soils. These stick-shaped rods encrust and retain the pore spaces open (Fig. 8a). Among other reasons, the brittleness of cement-stabilised clays is due to sudden collapse of these open spaces as soil is strained beyond peak. In Fig. 8b, fibres can be seen twining aggregates and passing through void spaces that in regions, are clearly lined with ettringite meshwork. The mediated brittleness in fibre-reinforced cement-stabilised clays can be attributed to void spaces intertwined by fibres. Despite the mediated brittleness, in Fig. 5c and Fig. 5d, addition of fibre to mixtures with 8 and 10 wt.% cement 'limited' the gain in strength. To put it more precisely, the compressive strength of 8 and 10 wt% mixtures without fibre is greater than similar mixtures with fibre. This curious observation is further discussed in the following section.

4.3 Morphological considerations

In Ghadr and Assadi-Langroudi (2020), we tracked the evolution of nanosilica precipitates in peat. We showed that colloidal particles of nanosilica tend to polymerise in solution, coagulate and form cubic blocks before precipitating on the surface of base soil particles (Fig. 4c). We also showed that, in their fully hydrated form i.e., shortly after precipitation and at low contents, precipitated nanosilica appears in form of flocs of distinct silica blocks (also Fig. 4c). As they age and at greater silica contents, flocs collide and merge to form larger, rounder, and smoother globules (Fig. 9a). They also form plates with upturned edges, shielding the clay platelets and other solids (Fig 9a). In Fig. 6, the direct association of peak strength with nbS content (up to 15 wt.%) and ageing is consistent with the evolution of nbS shape. In Fig. 7, the high rate of gain in strength at modest binder content ties in with distinct hydration products and silica globules (see Fig. 9a). As binder content and consequently nbS content increase, hydration products fail to set directly on surface of clay platelets and instead, they tend to sit within or on the nbS shield (Fig. 9b). This micromorphological transformation is consistent with diminished rate of gain in strength at higher binder content (Fig. 7).

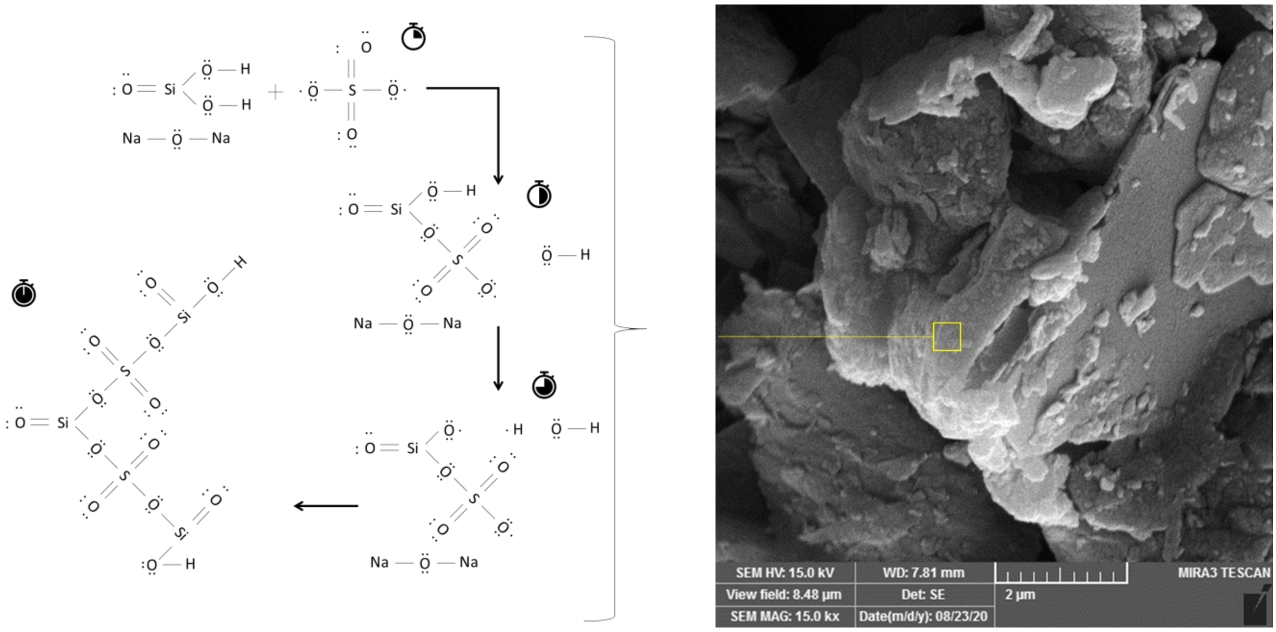


(a) Low total binder content (b) High binder content

Fig. 9 SEM micrographs of clay stabilised with C_3S-nbS mixtures

4.3 Manipulating the sulphates

Tannin acids supply high concentration of sulphates and low pH levels that can interrupt the cement hydration. However, presence of sulphates can become beneficial in nbS-mediated soils. Following administration of low nbS contents to soil, the colloidal solution precipitates on clay platelets, evaporate and form cubic crystals of partially hydrated nanosilica. On SEM micrographs, crystals appear on the face of clay platelets (F) as well as their mutual contact points (E). With time, interaction between sulphates and silica lend further strength to crystals. The hydroxyl tail of partially hydrated silica becomes liberated and replaced with sulphate via ligand exchange. The released hydroxide raises the pH of soil solution, leads to deprotonation of remaining hydroxides within partially hydrated silica and formation of complex SiO_2-SO_4 chains. Interactions are illustrated in Lewis structure form in Fig. 10 and further detailed in Assadi-Langroudi (2014).



(a) Lewis Structure of complex $[SiO_2.OH]_n$-[M-SO^2_4] chains: M stands for Metal

(b) Merged flocs into laminar shields

Fig. 10 Evolution of nbS in sulphate-rich environment

5. Conclusions

Highly organic clays are permanent stores of carbon and a medium for living microorganisms, flora and fauna. Mixing organic clays with Portland cement and densification is a universally common approach to engineering of organic clays. Removal of naturally open, flocculated structure of organic clays is a detriment to their ecological service provisions. Also, some organic components, in particular tannic acids imped or encourage the reversal of cement hydration.

This paper investigates scopes for use of a new alternative binder, a mixture of C_3S cement of 2.87 CaO/SiO_2 ratio and varied content, 0.5 wt.% of randomly distributed 19 µm in diameter 12 mm in length polymeric fibres, and a 30% colloidal crop-based highly basic, viscose, nanobiosilica with over 55% organic content for stabilisation of a slightly basic, sulphate rich, extremely plastic clay of 60% organic content. The principal objectives are to (i) increase the peak unconfined compressive strength above 0.5 MPa, (ii) to retain the strength near or above 0.5 MPa at strains up to 1.5 times the peak strain, (iii) to retain the naturally open, flocculated structure, (iv) to retain the naturally ductile stress-strain behaviour of organic clays.

Findings show, (i) The high Ca^{2+} concentration in C_3S cement allows production of hydration products, particularly C-S-H and ettringite. These provide durability for cementing products in hostile acidic environment, and remarkable improvement in strength at a cost of brittle failure; (ii) Small contents of fibre can relax the brittleness of C_3S-stablised clays, at a cost of more modest levels of gain in strength; (iii) Despite its high organic content, nanobiosilica, as a standalone stabiliser, can too be effective. Improvements to strength are modest but soil retains its natural ductile behaviour. (iv) sulphate in organic clays guarantee the durability of ettringites and interplays with nanobiosilica to form stronger poly-mineral bonds that gain further strength with time; (v) C_3S content of an effective binder can be relaxed through its partial replacement with nbS.

Acknowledgments

Authors would like to express thanks to the Geotechnical community of Urmia University, whom have been working on and documenting the many geo-environmental aspects of peat across the Urmia Wetland, over the past years. This particular research is conducted independently and did not receive funding from any institution.

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