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Key-Parameters in Chemical Stabilization of Soils with Multiwall Carbon Nanotubes

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Abstract: Chemical stabilization is one of the most successful techniques that has been applied to improve the geomechanical behavior of soil. Several additives have been studied to be a sustainable alternative to traditional additives (Portland cement and lime) normally associated with high cost and carbon footprint. Nanomaterials are one of the most recent additives proposed. This work is focused on one type of nanomaterial, multiwall carbon nanotubes (MWCNTs) with unique characteristics, applied to chemical stabilization of soils and aiming to identify the key-parameters affecting the stabilization improvement. It was found that a surfactant should be added in order to oppose the natural tendency of MWCNTs to aggregate with the consequent loss of benefits. The surfactant choice is not so dependent on the charge of the surfactant but rather on the balance between the concentration and the hydrodynamic diameter/molecular weight due to their impact on the geomechanical compression behavior. As time evolves from 7 to 28 days, there is a decrease in the geomechanical benefits associated with the presence of MWCNTs explained by the development of the cementitious matrix. MWCNTs applied in a proper concentration and enriched with a specific surfactant type may be a short-time valid alternative to the partial replacement of traditional additives.

Keywords: soil improvement; multiwall carbon nanotubes (MWCNTs); unconfined compressive strength tests; surfactant



Citation: Correia, A.A.S.; Casaleiro, P.D.F.; Figueiredo, D.T.R.; Moura, M.S.M.R.; Rasteiro, M.G. Key-Parameters in Chemical Stabilization of Soils with Multiwall Carbon Nanotubes. *Appl. Sci.* **2021**, *11*, 8754. <https://doi.org/10.3390/app11188754>

Academic Editor: Claudio De Pasquale

Received: 23 July 2021

Accepted: 17 September 2021

Published: 20 September 2021

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1. Introduction

Soil is the loose particulate natural material that covers the Earth's surface. Soil is a multiphase material containing an aqueous, gaseous and solid phase, each composed of inorganic and organic components. The interactions and relative proportions between the different components of the soil, and the arrangements, size and shape of the solid particles determine the soil's physical and chemical properties [1,2], and ultimately its geomechanical behavior (soil's response in terms of strength and deformability to external actions). In many cases, the soil does not meet the safety and stability requirements for construction, and ground improvement techniques are required [3–6]. This is the case of soft soils, characterized by exhibiting low strength and high deformability.

One of the most successful ground improvement techniques applied to soft soils is chemical stabilization with additives [7–10]. This ground improvement technique consists of in situ mixing additives to the soil, aiming to increase the soil's strength and decrease the soil's deformability. (There may be other objectives such as reducing permeability or immobilization of pollutants in the soil). The traditional additives most used in chemical

stabilization of soft soils are Portland cement and lime, applied alone or in combination in percentages ranging from 5% to 20% *w/w* (additive/soil) [11–13]. These additives have high costs and high environmental impacts associated to their production, which encourages the development of new additives. Industrial byproducts (e.g., slag, fly ash, rice ash), pozzolanic materials (e.g., fly ash, natural pozzolana, silica fume), biobased products (e.g., polymers, enzymes) and nanomaterials (e.g., carbon nanotubes, carbon nanofibers, nano-ashes, nanoclays) are some examples of promising additives that may be used as a total or partial replacement of the traditional additives [11,13–20].

Additives consisting of extremely fine particles (nanomaterials) are particularly attractive for use as replacement of part of cementitious additives, resulting in environmental, technical and economic advantages [21–23]. Due to extraordinary properties of carbon nanotubes (CNTs) (fine structure, ultrahigh specific surface, very high strength and moduli of elasticity, elastic and ductile behavior [24–28]), they have a great potential to be used as an additive in chemical stabilization of soils, replacing part of the cementitious main additive. However, due to CNT morphology and very high aspect ratio, CNTs have a natural tendency to aggregate, resulting in the loss of their beneficial properties [29,30]. Different strategies have been proposed to minimize this problem, including mechanical methods (e.g., ultrasonic energy applied to disperse CNTs in suspension) and chemical methods (e.g., functionalization of CNT surface by the addition of surfactants/polymers to the system), among others. The introduction of surfactants has a double advantage since it allows the dispersion of the CNTs and other additive particles, while at the same time minimizes ultrasound energy requirements.

The application of CNTs to geotechnics is still at the laboratory development and proof-of-concept stage, with few studies published thus far, being possible to conclude the following: (i) The introduction of CNTs in a content of 0.2% up to 1% of soil's dry weight is able to increase slightly the specific gravity, dry density and pH [31]; increase the plasticity index; increase the compression and swelling indices and reduce the hydraulic conductivity of the soil [32]. (ii) Mixing a clayey sand with CNTs applied in a content of 0.05–3% by weight of the soil promotes an increase of the compressive strength of the composite material up to 120% when compared with the original clayey soil, and increases the cohesion while decreasing the friction angle [33]. (iii) The combination of Portland cement with CNTs in a content of 0.001% to 0.01% Portland cement's dry weight has the potential to increase the unconfined compressive strength and the Young's modulus of the composite material up to 77% and 155%, respectively [8,34]. These studies show that it is possible to conclude that CNT presence in a soil matrix have an effect on the physical structure (reducing the interparticle spacing and nanoreinforcing the soil), and on the chemical reaction development when a cementitious material is added, allowing the construction of a stronger and stiffer soil skeleton matrix, therefore improving the geomechanical behavior of the composite material [34].

Despite the research to date, the impact of CNTs in chemically stabilized soil matrixes has not been properly studied. Furthermore, the fundamental parameters and their effect on the geomechanical behavior of the composite material have not been clearly identified and quantified. Thus, the present work aims to identify and evaluate the impact of some of the most important parameters on the geomechanical behavior of a chemically stabilized soil that contains carbon nanotubes. The surfactant type and concentration parameters, time and CNT concentration are studied in this work, aiming to quantify their importance on the geomechanical behavior of the composite material. These parameters and their effects are the focus and main novelty of this work, advancing the existing knowledge of the composite materials.

2. Methodology

2.1. Testing Plan

In order to determine the key-parameters on the geomechanical behavior of a soil chemically stabilized and containing carbon nanotubes, the following experimental testing

plan was designed: (i) Unconfined compressive strength (UCS) tests were performed on samples stabilized with four different surfactant types, varying in charge (nonionic and cationic), molecular weight and concentration (ranging from 0.1 to 3%). (ii) UCS tests were performed on samples stabilized with a CNT concentration of 0.001% and 0.01%. (iii) UCS tests were made on stabilized samples with different curing times (7 and 28 days). Table 1 summarizes the testing plan. The experimental work was complemented with particle size distribution tests to characterize the quality of CNT dispersions and with leaching tests to assure that CNTs are not released from the chemically stabilized soil matrix.

Table 1. Experimental testing plan.

Surfactant		CNTs		Time
Name	Conc. (%)	Conc. (%)		(Days)
-	-	-	-	7/28
		0.001	-	
		0.01	-	
Viscocrete	3	-	-	7/28
		0.001	-	
		0.01	-	
Glycerox	0.5/1/2	-	-	7
		0.001	-	
		0.01	-	
Amber 2001	0.1 */0.5/1 */2	-	-	7 *
		0.001	-	
		0.01	-	
Amber 4001	0.5/1/2/3	-	-	7
		0.001	-	
		0.01	-	

conc. = concentration; * there is a test for a time of 28 days but without CNTs.

2.2. Materials

A soil collected in central Portugal, near the city of Coimbra, was used in the experimental study. The soil is mainly composed of silt (~66%) with some clay (8–12%) and sand (17–22%) particles, having in its composition a high organic matter content (9.3%), which is mainly responsible for the plasticity characteristics of the soil (liquid limit $w_L \approx 71\%$ and plastic limit $w_P \approx 43\%$). The natural soil exhibits a high water content (80.9%), high void ratio (2.1) and low unit weight (14.6 kN/m^3), and is classified by the Unified Soil Classification System [35] as OH, organic silt with high plasticity [36–38]. These characteristics give the soil a poor geomechanical behavior (low strength and high deformability); thus, a ground improvement technique should be adopted to allow for any construction on it [39]. In the present work, chemical stabilization was selected to improve the soil properties by mixing the soil with a binder and a suspension of “properly” dispersed carbon nanotubes. Although the soil is slightly acid ($\text{pH} \approx 4.5\text{--}5.3$), which may restrain some binder reactions, it exhibits high silica (~62%) and alumina (~16%) content, allowing a long-term strength improvement [7,8].

The soil was chemically stabilized with Portland cement type I 42.5 R, applied in a quantity of 175 kg/m^3 (kilos per cubic meter of soil). Table 2 presents the main characteristic of the cement particles. The high specific surface of the cement particles and the fact that they are slightly negatively charged should be highlighted.

Table 2. Characteristics of cement particles (Portland cement type I 42.5 R).

CaO (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MgO (%)	SO ₃ (%)	Cl ⁻ (%)	S (m ² /kg)	Z (mV)
62.8	19.2	4.9	3.2	2.5	3.4	0.01	349	-2.14

S = specific surface; Z = zeta potential (evaluated by electrophoretic light scattering).

Carbon nanotubes were selected as an additive for the chemical stabilization of the soil, aiming to improve the geomechanical behavior of the composite material while promoting a reduction of the quantity of Portland cement added. Multiwall carbon nanotubes (MWCNTs) were chosen for the present work mainly due to economic factors; MWCNTs are significantly less expensive than singlewall carbon nanotubes and, so far, only MWCNTs are produced at an industrial level. According to data provided by the manufacturer, MWCNTs CN7000 have a mean diameter of 9.5 nm, a mean length of 1500 nm, a mean specific surface of 275,000 m²/kg (1000 times greater than cement particles) and are composed of 90% pure carbon with some metal oxides (10%). MWCNT characterization was complemented with the evaluation of its density (1.7 g/cm³) and charge (-25.2 mV) [8,21]. MWCNTs were applied in two small concentrations (0.001 and 0.01% *w/w* referred to the dry binder mass) to keep costs under control.

For the present work, four different surfactant types were selected: two commercial ones (Viscocrete and Glycerox supplied by Sika and Lubrizol, respectively) and two other noncommercial types (Amber 2001 and Amber 4001 developed by Aquatech), varying in charge (nonionic and cationic), molecular weight and concentration (ranging from 0.1 to 3%), as presented in Table 3. The choice of surfactants was determined by the charge of the additive (-25.2 and -2.14 mV for MWCNTs and cement particles, respectively), so cationic or nonionic surfactant types were selected, differing in molecular weight and size. The surfactants were added with the aim to disperse “properly” the MWCNTs particles, avoiding the loss of their beneficial properties. It is important to notice that the surfactants also have the potential to disperse the cement particles, justifying the tests without MWCNTs, included in the experimental testing program (Table 1).

Table 3. Characteristics of surfactants [36–38].

Surfactant	Market Condition	Charge (-)	Z (mV)	D _z (nm)	MW (kDa)
Viscocrete	commercial	nonionic	-2.8	4.65	242
Glycerox	commercial	nonionic	~0	41.93	4265
Amber 2001	noncommercial	cationic	66.7	170.84	1155
Amber 4001	noncommercial	cationic	-	5.65	54

Z = zeta potential (evaluated by electrophoretic light scattering); D_z = hydrodynamic diameter (evaluated by dynamic light scattering); MW = molecular weight (evaluated by static light scattering).

2.3. Sample Preparation and Tests

The samples of the soil chemically stabilized with Portland cement additivated or not with MWCNTs were prepared following the laboratory procedure presented in Figure 1.

After the soil homogenization, a representative sample was collected (phase I). A slurry composed of Portland cement (phase II) plus MWCNTs dispersed with the aid of surfactant (phase II.C) or not (phase II.A) was prepared. The MWCNTs were dispersed with ultrasonic energy, using an ice bath with water flux to control the temperature, applied to an aqueous suspension of MWCNTs (phase II.A) or to an aqueous solution of surfactant with MWCNTs (phase II.C). The ultrasounds were applied using a probe-sonicator (Vibracell 501 from Sonics), during 5 min with a frequency of 20 Hz and power of 500 W. The quality of the MWCNTs dispersion was evaluated by the particle size distribution analysis obtained using DLS (the smaller the particle size, the better the quality of dispersion). As surfactants can also promote the dispersion of binder and/or soil particles, tests with only a surfactant solution, cement and soil (phase II.B) were prepared. The water present in

the slurry/aqueous suspension or solution increases the water content from the natural value (80.9%) to 113%. Afterward, the materials were mechanically mixed (phase III) and the paste produced was introduced in PVC molds in six layers (phase IV). Each layer was slightly compressed with a circular plate and vibrated with the help of a hand drill to remove possible air bubbles that may exist in the paste. Two geotextile filters were applied at the bottom and top of the sample. After curing under water for a period of 7 or 28 days (phase V) the samples were demolded and carefully cut to the final height of 76 mm (phase VI). Finally, the sample was placed on the compression load frame (Tristar 5000 from Wykeham Farrance) and the UCS test was performed at a constant strain rate of 0.76 mm/min (in agreement with BSI 1377-7 [40] and ASTM D2166 [41]). During the test, automatic readings were taken from the load cell and the vertical displacement transducer, allowing the definition of the stress–strain curve. All the tests were repeated twice to guarantee the reliability of the results. In order to assure that MWCNTs were not released from the chemically stabilized soil matrices, leaching tests were performed. More details can be found in Casaleiro [36], Figueiredo [37] and Moura [38].

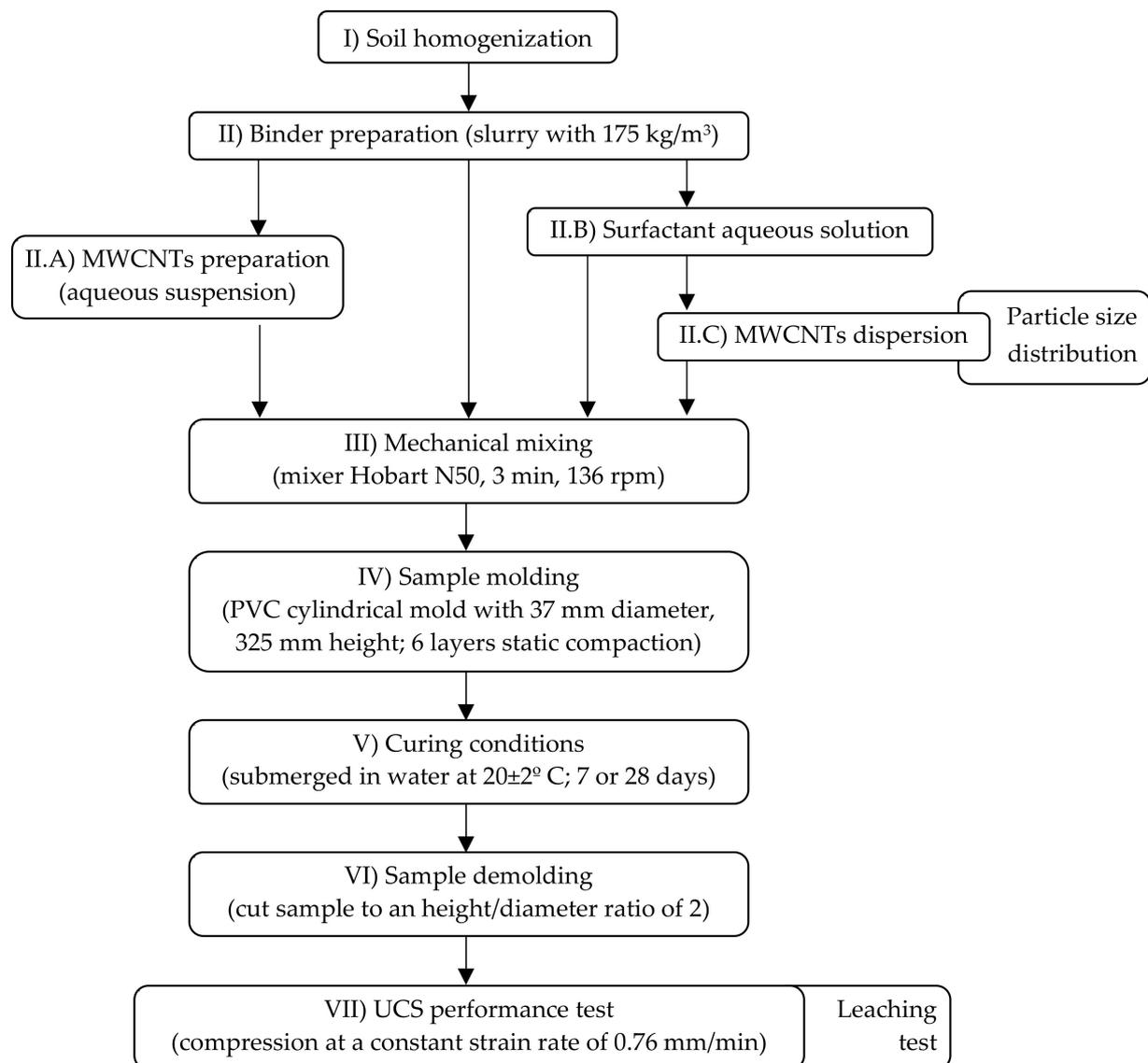


Figure 1. Laboratory procedure for preparation of soil samples chemically stabilized with Portland cement additivated or not with MWCNTs.

3. Results and Discussion

The results present some scattering between the samples tested for each different test condition due to the experimental nature of the study. Nevertheless, only the tests that comply with the conformity criterion ($\pm 15\%$ of the variation of the unconfined compressive strength compared to the average value) were accepted.

The impact of the different parameters (surfactants, MWCNTs concentration, time) on the chemically stabilized soil behavior are expressed by the unconfined compressive strength improvement factor (IF), defined as the ratio between the unconfined compressive stress (q_u) of a specific test condition and the unconfined compressive strength of the reference test ($q_{u\ max}^{ref}$, for the test condition without surfactants or MWCNTs):

$$IF = \frac{q_u}{q_{u\ max}^{ref}} \quad (1)$$

The results are presented, preferably, as a function of the strength improvement factor, allowing in this way a direct reading of the impact of the parameters under study on the chemically stabilized soil behavior.

Figure 2 presents the stress–strain curves for the reference tests at 7 and 28 curing days. It should be noted that independent of the curing time, 7 and 28 days, both tests, T1 and T2, show very similar stress–strain curves, demonstrating good reproducibility of the laboratory procedure. As expected, the strength and stiffness increase with time as a result of the development of the physicochemical reactions of the Portland cement responsible for producing a stronger stabilized matrix [24,39,42–45].

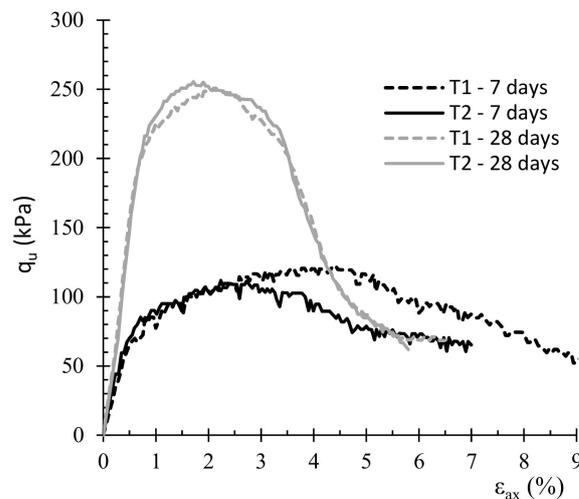


Figure 2. Stress–strain curves for the reference test conditions (soil chemically stabilized with Portland cement).

3.1. Effect of Surfactant Type

Figures 3 and 4 summarize the results of the effect of the surfactant type added to the chemically stabilized soil samples with a curing time of 7 days. With the exception of the higher concentrations of the surfactant Amber 4001, the addition of the surfactants has a positive impact on the geomechanical behavior of the stabilized soil, proving that the surfactant has the potential to better disperse the binder and/or the soil particles, thus, allowing the construction of a denser and stronger solid skeleton matrix. The best result was obtained with the surfactant Viscocrete ($IF = 1.55$), a nonionic surfactant type applied in a concentration of 3%. The results obtained for the other nonionic surfactant (Glycerox) are also positive but with lower strength improvement factors (IF ranging from 1.07 to 1.21). However, the IF increases with the Glycerox concentration, suggesting that for a higher Glycerox concentration better results could be obtained. This result may be explained by

the fact that Viscocrete presents a smaller hydrodynamic diameter and molecular weight than Glycerox; thus, a smaller size of the surfactant molecules allows better adsorption on the surface of the solid particles (soil and binder), ensuring better dispersion. This is also valid when comparing the two cationic surfactants, justifying the better results with the Amber 4001, which has a smaller hydrodynamic diameter and molecular weight than Amber 2001. Moreover, the fact that the particle surface is not so much covered by surfactant when lower molecular weight and hydrodynamic diameter surfactants are used, may favor the cementitious reactions.

When comparing the two cationic surfactants (Amber 2001 and Amber 4001) with the nonionic surfactants for equal concentrations, it may be seen that for lower concentrations (0.5% and 1%) the best results are obtained with the cationic surfactants. However, for higher concentrations, the results of the Amber 2001 (2% conc.) are of the same order as those for Glycerox while for Amber 4001 (2% and 3% conc.) the results are negative ($IF < 1.0$) and lower than those for Glycerox and Viscocrete, respectively, for a concentration of 2% and 3%. Thus, the surfactant choice is not so dependent on the surfactant charge but rather on the balance between the concentration and the hydrodynamic diameter/molecular weight.

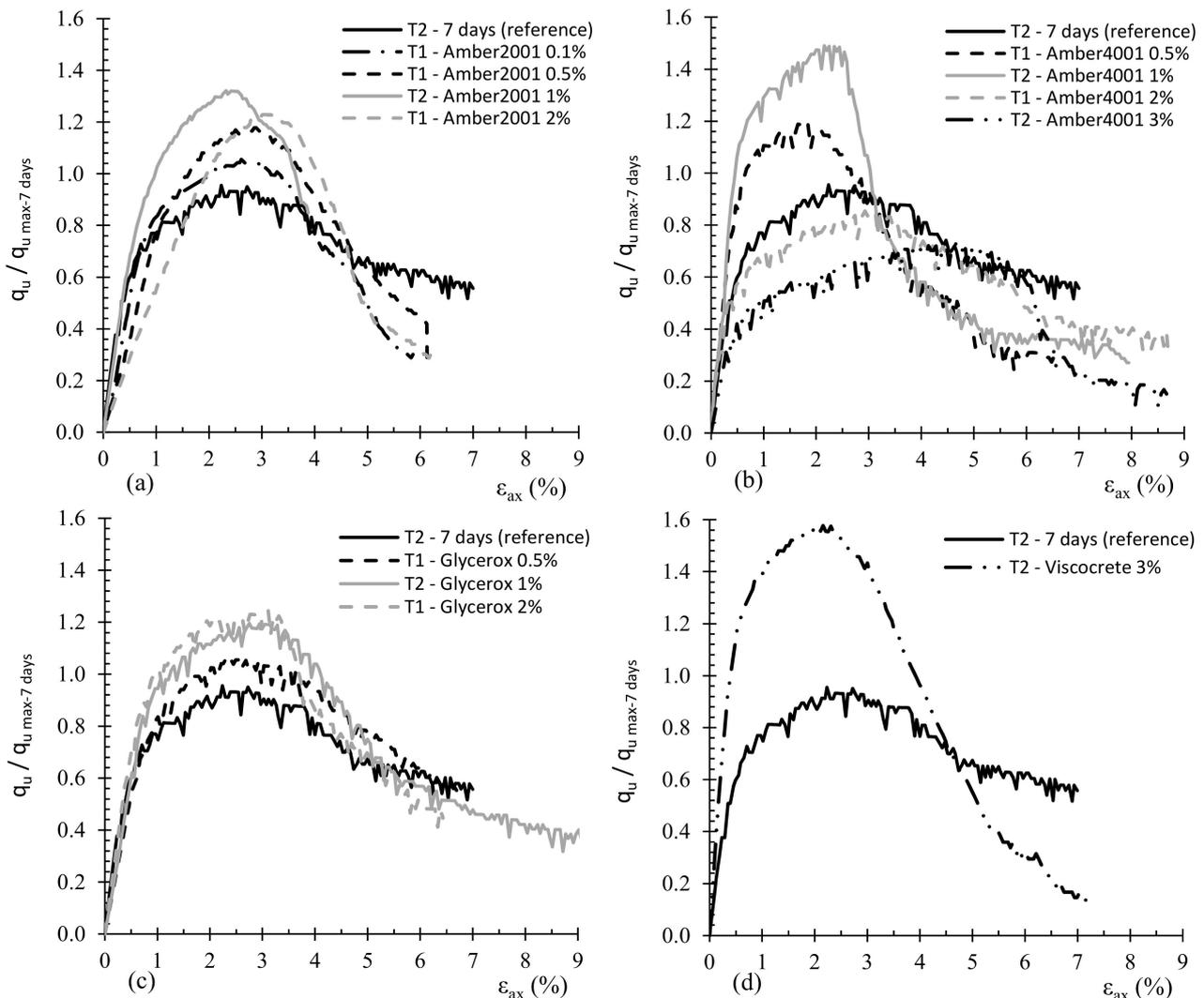


Figure 3. Stress–strain normalized curves (for samples with 7 curing days) for the stabilized soil with only a surfactant solution of (a) Amber 2001, (b) Amber 4001, (c) Glycerox and (d) Viscocrete.

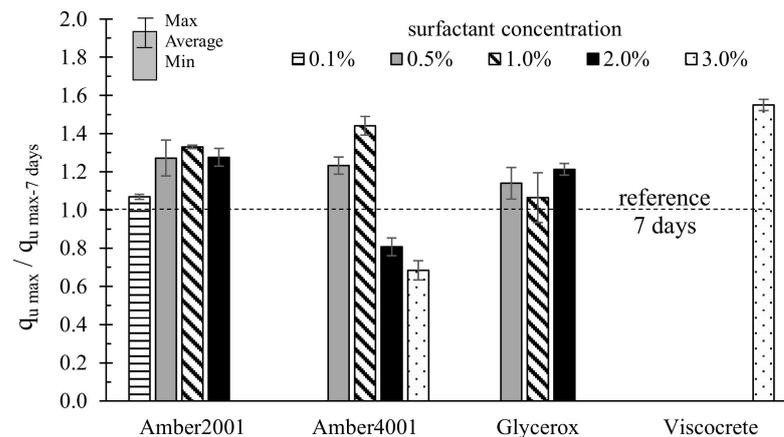


Figure 4. Strength improvement factor (for samples with 7 curing days) for the stabilized soil with only surfactant solutions.

As time evolves, the impact of the surfactant on the geomechanical behavior of the chemically stabilized soil may change since the surfactant presence may have effect on the time development of the physicochemical reactions of the Portland cement. To study this effect, samples were prepared with nonionic and cationic surfactants for the best concentrations, i.e., Viscocrete and Amber 2001 applied in a concentration of 3% and 1%, respectively. From the results (Figure 5), it may be seen that the cationic surfactant now has a negative effect while the nonionic surfactant still presents a positive but smaller effect on the geomechanical behavior of the chemically stabilized soil. Indeed, as the cementitious products are produced over time the solid matrix becomes denser, justifying the decrease in the importance of the surfactant. The decrease of the strength improvement factor is higher for the surfactant with larger molecule size (Amber 2001, IF decreases from 1.33 to 0.81), which may be explained by two factors: (i) surfactants with larger molecules potentially form micelles for lower surfactants concentrations, making the occurrence of cementitious reactions more difficult; (ii) surfactants with larger molecules adsorbed on the surface of solid particles may prevent the establishment of some cementitious bonds, thus promoting a solid matrix with less strength. Nevertheless, more tests should be performed for other surfactants and concentrations in order to deeper understand the surfactant effect over time.

3.2. Effect of MWCNTs

Figure 6 presents the results of the chemically stabilized soil samples additivated with MWCNTs dispersed in aqueous solution (without surfactant) for curing times of 7 and 28 days. It is clear that independent of the curing time the addition of the MWCNTs has a negligible effect on the geomechanical behavior of the chemically stabilized soil. This result contradicts previous studies with carbon nanotubes where it was found that the addition of a small concentration of CNTs has a significant impact on the geomechanical properties of a soil [8,32–34]. These results make clear that more important than the introduction of MWCNTs in a soil matrix is the need to ensure that they are properly dispersed in order to avoid the loss of their beneficial properties. Thus, it is crucial to add to the MWCNTs aqueous suspension a surfactant that may help in the dispersion process. Figure 7 shows several aqueous suspensions containing MWCNTs with and without surfactants, all dispersed with ultrasonic energy. The MWCNTs suspension without surfactant (Figure 7a) has aggregates clearly visible to the naked eye, whereas in the case where surfactant was added at the lowest concentration (Figure 7b,c) homogeneous suspensions are present.

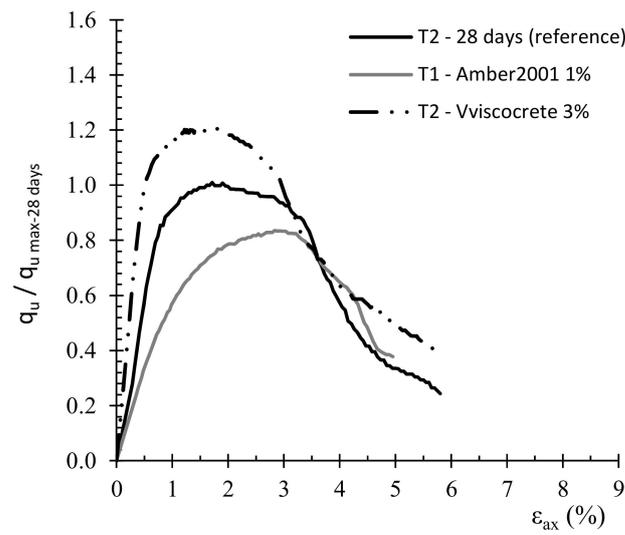


Figure 5. Stress–strain normalized curves (for samples with 28 curing days) for the stabilized soil with only a surfactant solution of Amber 2001 (conc. of 1%) and Viscocrete (conc. of 3%).

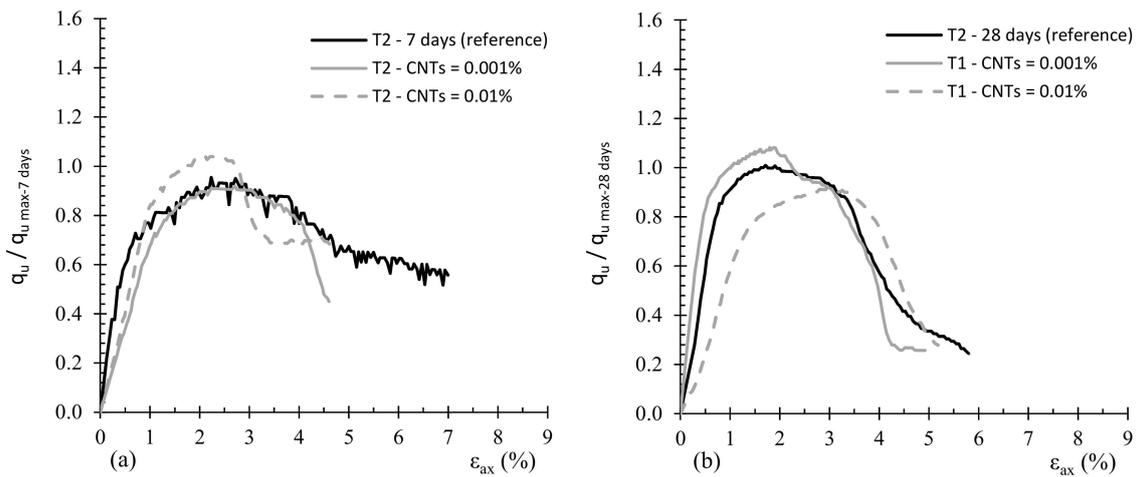


Figure 6. Stress–strain normalized curves for the stabilized soil additivated with MWCNTs and no surfactant for samples with (a) 7 curing days and (b) 28 curing days.

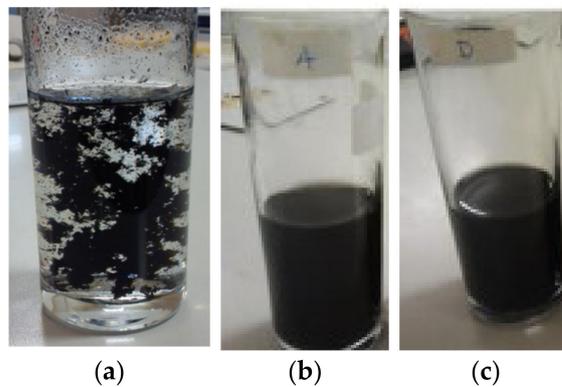


Figure 7. Photographs of MWCNT suspensions immediately after ultrasonication for a MWCNT concentration of 0.01%: (a) sample without surfactant, (b) sample with Glycerox at concentration of 0.5% and (c) sample with Amber 4001 at concentration of 0.5%.

Figures 8 and 9 summarize the results of the impact of adding MWCNTs (in concentrations of 0.001% and 0.01%) dispersed in a solution of surfactants to chemically stabilized soil samples for a curing time of 7 days. With the exception of the higher concentrations of the surfactant Amber 4001, the addition of MWCNTs for both concentrations (0.001% and 0.01%) dispersed in a solution of surfactants have a positive impact on the geomechanical behavior of the stabilized soil, proving that the addition of MWCNTs to a chemically stabilized soil can only be effective if the MWCNTs are “properly” dispersed.

The best results were obtained with the surfactants Amber 4001, Viscocrete and Glycerox, applied in concentrations of 1%, 3% and 2%, respectively, independent of the MWCNTs concentration ($IF = 1.76, 1.62$ and 1.63 for a MWCNTs conc. of 0.01%; $IF = 1.66, 1.63$ and 1.48 for a MWCNTs conc. of 0.001%). The results prove that the size of the surfactant molecules (Table 3) have a major role on the MWCNTs dispersion process (Table 4) and, ultimately, on the geomechanical behavior of the composite materials. Indeed, the smaller the size of the surfactant molecules, the better the quality of the dispersion (Table 4), i.e., smaller surfactant molecules adsorb more easily on the surface of the solid particles (MWCNTs, binder and soil), ensuring better dispersion and geomechanical behavior. These results agree with previous findings regarding the surfactant effect when no MWCNTs were added, but now the presence of MWCNTs enhances even more the strength improvement factor. However, it should be emphasized that better geomechanical behavior is not always associated with better MWCNTs dispersion because the medium where dispersion occurs is different; the characterization of MWCNT dispersion occurs in an aqueous medium enriched with surfactant while for the UCS tests in the medium there are chemically reacting cement particles and soil particles.

It should be noted that as the surfactant concentration increases, there may be formation of micelles when the critical micelle concentration (CMC) is exceeded, an effect that potentially may happen more easily given a larger size of the surfactant molecules. As seen from Table 4, for the surfactants with largest molecule sizes (Glycerox and Amber 2001), the hydrodynamic diameter of the MWCNTs dispersion increases slightly for a Glycerox concentration above 1% (suggesting the CMC is somewhat between 1% and 3%), while for the surfactant Amber 2001 the hydrodynamic diameter always increases with surfactant concentration (suggesting the CMC can be less than 0.5%). However, this is compatible with good MWCNTs dispersion since the formation of micelles is not necessarily detrimental for particle dispersion [8]. Thus, as stated before, the surfactant choice should be based on the balance between the concentration and the hydrodynamic diameter/molecular weight.

The surfactant Amber 2001 exhibits the worst performance since it has the largest hydrodynamic diameter, leading to MWCNTs dispersions of bad quality, as it may be seen from Table 4. The other cationic surfactant (Amber 4001) has an effect on the geomechanical behavior of the stabilized soil that depends on the surfactant concentration. For concentrations up to 1% (probably below the CMC), there is a significant beneficial impact that may be attributed to the cationic charge of the surfactant Amber 4001, which favors adsorption to MWCNTs and binder particles, thus promoting better dispersion and geomechanical behavior. On the contrary, for higher surfactant concentrations (2% and 3%, probably above the CMC) the MWCNT and binder particle dispersion is of poor quality, producing a negative effect in terms of geomechanical behavior of the chemically stabilized soil additivated with MWCNTs. Generally, the Glycerox surfactant presented better results regarding the geomechanical behavior of stabilized soils additivated with MWCNTs, especially for concentrations of 2% or higher. This can be associated with better dispersion of MWCNTs obtained with this surfactant (see Table 4). Indeed, it was observed that for higher surfactant concentrations (2% and 3%) a nonionic surfactant type (Glycerox and Viscocrete) assures better geomechanical behavior as long as it has a good MWCNTs dispersion.

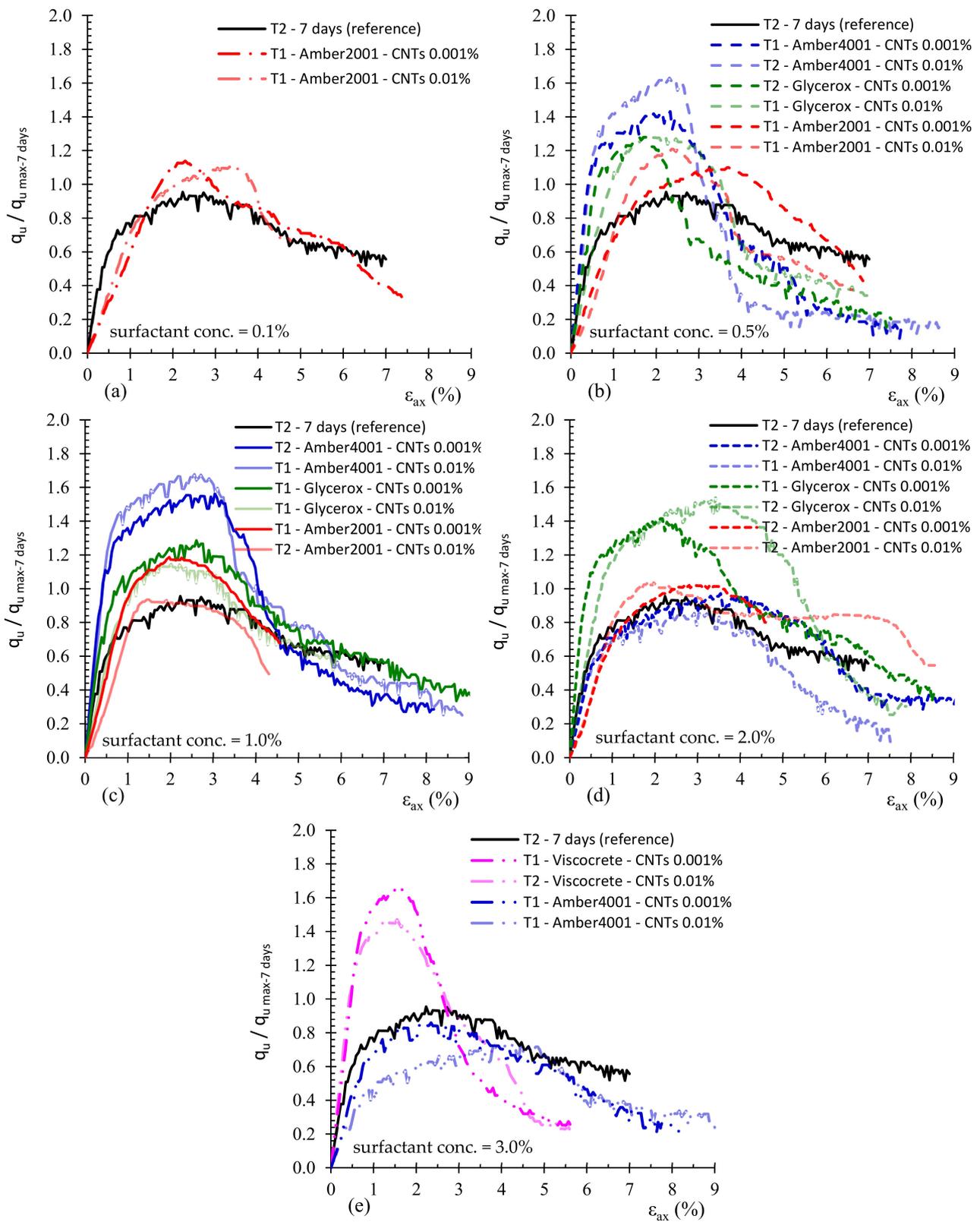


Figure 8. Stress–strain normalized curves (for samples with 7 curing days) for the stabilized soil with MWCNTs suspensions for different surfactants applied in concentrations of (a) 0.1%, (b) 0.5%, (c) 1.0%, (d) 2.0% and (e) 3.0%.

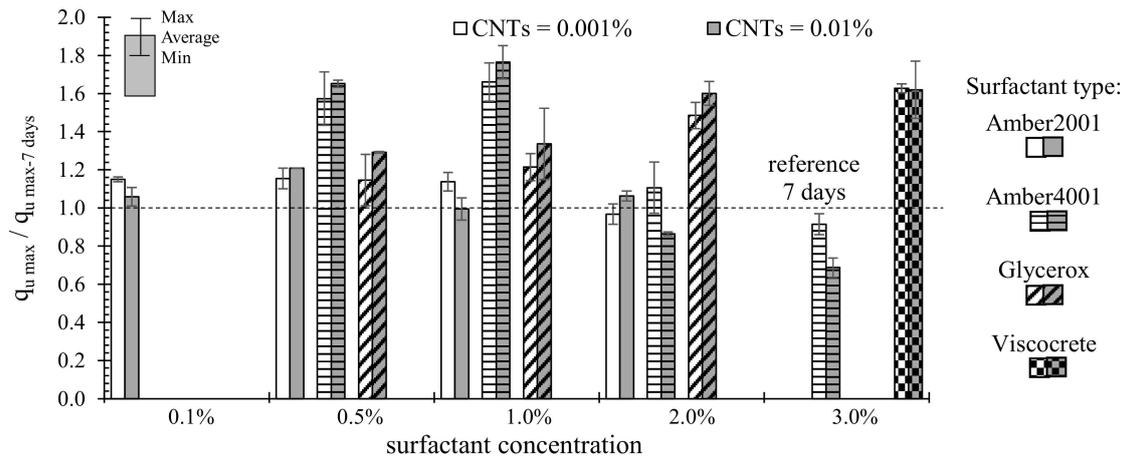


Figure 9. Strength improvement factor (for samples with 7 curing days) for the stabilized soil with MWCNT suspensions for the surfactants studied, applied in different concentrations.

Table 4. Dispersion characterization of MWCNTs suspensions.

Surfactant		D _z (for MWCNTs = 0.001%/0.01%)	
Name	Conc. (%)	(nm)	
Viscocrete	3	155.1/119.5	
	0.5	-/197.2	
Glycerox	1	-/167.6	
	3	-/175.2	
	0.1	-/-	
Amber 2001	0.5	548.0/684.5	
	1	-/718.2	
	2	-/954.2	
Amber 4001	0.5	-/521.5	
	1	-/322.9	
	3	-/316.8	

conc. = concentration; D_z = hydrodynamic diameter (evaluated by dynamic light scattering).

Generally, better results were obtained for higher MWCNT concentrations, which may be explained by the fact that the presence of a higher number of nanoparticles will nanofill the matrix voids, allowing the development of a denser stabilized matrix. At the same time, due to the extraordinary mechanical properties of the MWCNTs (very high strength and stiffness), their presence in a higher quantity in a stabilized matrix will promote the enhancement of the geomechanical behavior since MWCNTs are bonded to the cementitious products produced by the Portland cement. In summary, when the MWCNTs are dispersed in a soil-binder matrix they may act as a nanofiller and nanoreinforcement, promoting a denser and stronger stabilized matrix.

As observed for the effect of surfactant, the impact of the MWCNTs on the geomechanical behavior of the chemically stabilized soil decreases as time evolves for all the surfactants and concentrations studied, independent of the quantity of MWCNTs (Figure 10). As the curing time evolves from 7 to 28 days, the cationic surfactant no longer has a positive effect on the geomechanical behavior, presenting a detrimental effect: for a MWCNTs concentration of 0.001%, the strength improvement factor decreases from 1.15/1.14 to 0.97/0.89 for surfactant concentration of 0.1%/1%, respectively; while for the case of a MWCNTs concentration of 0.01% the IF decreases from 1.06/0.99 to 0.93/0.78 for the same surfactant concentrations. A similar observation can be made for the nonionic surfactant

Viscocrete, where the IF decreases from 1.63 at 7 days to 1.36 at 28 days. Even though there is a decrease, in the case of the surfactant Viscocrete, the effect at 28 days is still positive contrary to what is observed for the Amber 2001, which may be related to the size of surfactant molecules. Indeed, Viscocrete is characterized by molecules of smaller hydrodynamic diameter than Amber 2001 (Table 3); thus, Viscocrete is less likely to form micelles that may hinder the occurrence of cementitious reactions and at the same time the smaller size of the Viscocrete molecules allow the bonding of the cementitious products to the surface of the solid particles (MWCNTs and soil), thus promoting a denser and stronger solid matrix. The relative decrease of the effect of MWCNTs with time is explained by the development over time of the physicochemical reactions of the Portland cement producing a greater quantity of cementitious products. Thus, with time the matrix becomes denser and stronger and, as a consequence, the relative impact of MWCNTs presence decreases.

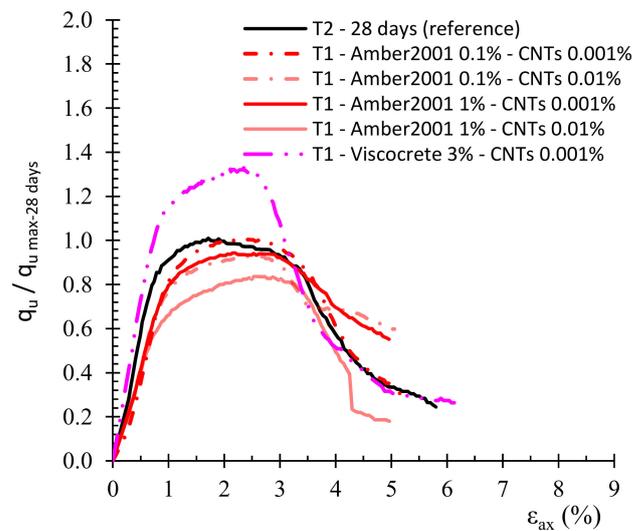


Figure 10. Stress–strain normalized curves (for samples with 28 curing days) for the stabilized soil with MWCNTs suspensions of the surfactant Amber 2001 (conc. of 0.1% and 1%) and Viscocrete (conc. of 3%).

One important issue related with the application of CNTs is their impact on environment if CNTs are released, namely, on human life, animals and plants. In order to investigate a possible release of MWCNTs from the stabilized soil matrices, leaching tests on chemically stabilized soil samples additivated with MWCNTs dispersed in a surfactant solution were done at 1, 4, 7 and 14 curing days. These tests were complemented with optical microscope images and SEM images of the leachate. Tests were performed for the “worst scenario”, i.e., adding the highest quantity of MWCNTs (0.01%) dispersed in an Amber 2001 solution (conc. = 0.1%). As seen in Figure 11, two kinds of materials were identified in the SEM images: needle-shaped materials are calcium silicate associated with the Portland cement reactions with water, and materials in the form of irregular polyhedrons are soil particles. By analysis of Figure 11, it can be concluded that there are no traces of MWCNTs in the leachate, proving that the MWCNTs are entrapped in the stabilized soil matrix. In summary, the analyses from the leachate resulting from leaching tests, it is concluded that the amount of material released is not significant and does not contain traces of MWCNTs.

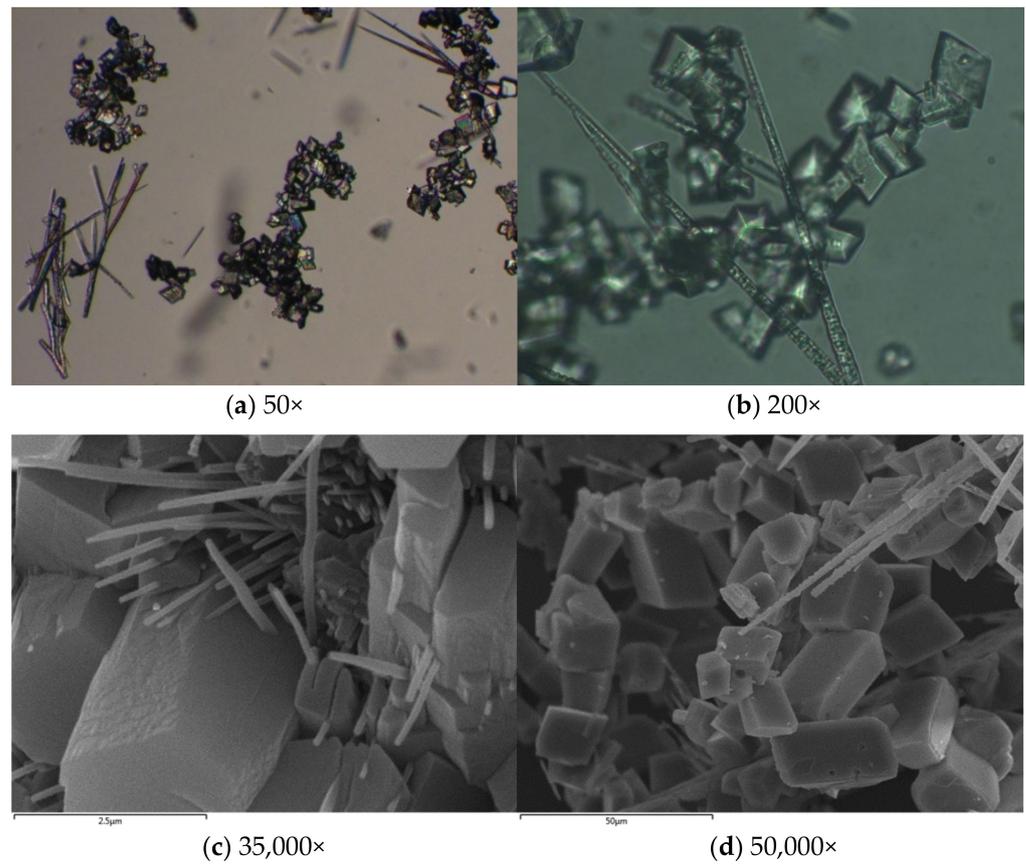


Figure 11. Optical and SEM images of the leachate at 7 days from a chemically stabilized soil samples additivated with MWCNTs (conc. = 0.01%) dispersed in a solution of Amber 2001 (conc. = 0.1%) with 7 curing days: (a,b) optical images and (c,d) SEM images.

4. Conclusions

The present work is a contribution to identify the most important or fundamental parameters that control the geomechanical behavior of a chemically stabilized soil additivated with MWCNTs dispersed or not in a surfactant solution. Based on the laboratory tests performed, it was found that a simple addition of MWCNTs to the stabilized soil does not produce any improvement of its geomechanical behavior since the nanoparticles are in an aggregate condition, which inhibits its ability to take advantage of the extraordinary properties of MWCNTs. The introduction of a surfactant to the chemically stabilized soil promotes the dispersion of the cement and soil particles, allowing the development of a denser and stronger solid skeleton matrix, which is reflected in an improvement of the geomechanical behavior up to 155% compared with the reference test. When the MWCNTs are combined with a surfactant solution and good MWCNTs dispersion is achieved, there is an enhancement of the geomechanical behavior of the stabilized soil up to 176% or 185% (for a MWCNTs concentration of 0.001% or 0.01%, respectively) compared with the reference test. Thus, for the concentrations examined, the MWCNTs concentration seems not to be a fundamental parameter since similar improvements can be achieved for a concentration that is 10 times lower. On the contrary, the characteristics of the surfactant seem to be a fundamental parameter affecting the geomechanical behavior of the stabilized soil enriched with MWCNTs. Indeed, the surfactant choice should depend on the balance between the concentration and the hydrodynamic diameter/molecular weight. A smaller size of the surfactant molecules allows better adsorption on the surface of the solid particles (MWCNTs, binder and soil), ensuring better dispersion without interfering with the cementitious reactions.

As time evolves from 7 to 28 curing days, a relative decrease of the effect of surfactants and MWCNTs on the geomechanical behavior of stabilized soil samples was observed, explained by the fact that the physicochemical reactions of the Portland cement develop with time, producing a greater quantity of cementitious products responsible for making the stabilized matrix denser and stronger and, as a consequence, the additives importance diminishes. Thus, time seems to be a fundamental parameter since better results are achieved for shorter times.

In summary, the addition of MWCNTs, “properly” dispersed, with the objective to contribute to the chemical stabilization of a soil, has potential to improve its geomechanical behavior. Thus, for the same level of unconfined compressive strength, MWCNTs applied in a proper concentration and enriched with a specific surfactant may provide a quick and valid alternative to the partial replacement of Portland cement. Moreover, it was demonstrated from the leaching tests that no traces of MWCNTs were observed in the leachate, proving that the MWCNTs are entrapped in the stabilized soil matrices, thereby not presenting a risk for people, animals or plants.

Author Contributions: P.D.F.C., D.T.R.F. and M.S.M.R.M. conducted the experimental investigation; A.A.S.C. prepared the first draft of the manuscript and was responsible for the conceptualization, validation and supervision of the research, and review and editing of the manuscript; M.G.R. was co-responsible for the conceptualization, validation and supervision of the research and participated in the review and editing of the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research received financial support from the Strategic Research Centre (CIEQPFP) Project UIDB00102/2020, funded by FCT (Fundação para a Ciência e Tecnologia), Portugal.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: The authors would like to express their thanks to CIMPOR and AQUATECH for supplying the binder and the cationic surfactants, respectively.

Conflicts of Interest: The authors declare no conflict of interest.

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