CHEMICAL ENGINEERING TRANSACTIONS

VOL. 84, 2021

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Paolo Ciambelli, Luca Di Palma

ISBN 978-88-95608-82-2; **ISSN** 2283-9216

Experimental Analysis of Hydraulic Characteristics of Coarse-grained Soil Treated with Natural-based Nanomaterials

Matilde Cinelli[a,*], Diego Sebastiani[a], Quintilio Napoleoni[b]

[a] GEEG Geotechnical and Environmental Engineering Group, Startup of Sapienza University of Rome, corso d'Italia, 97, 00198, Rome, Italy
[b] Dept. of Civil, Constructional and Environmental Engineering of Sapienza University of Rome, via eudossiana, 18, 00184, Rome, Italy
matilde.cinelli@geeg.it

In the last decades the interest in nanomaterials considerably increased due to the development of new technologies of micronization. The prospect of achieving large amounts of nanomaterials from natural bulk materials allows to evaluate the replacement of cement in low-pressure injection for geotechnical soil stabilization. The aim of the research activities was to point out the effectiveness of the injection of nanomaterials in the decrease of permeability in coarse-grained soils. In this study, nanomaterials from sand, clay and graphene were used to create the mix design. In order to reach the goal, a first step was the characterization of nanomaterials and sand used as matrix, then shape and number of samples were defined and finally constant head test was carried out to provide hydraulic conductivity. The results confirmed that the proper injection of nanoparticles-based mixture could be considered a sustainable solution useful to reduce the permeability of coarse-grained soil.

1. Introduction

According to the recent development of micronization techniques, large amounts of nanomaterials are now available for engineering applications. The micronization process is defined as the particles size reduction to less than 10 μm achieved through different mechanism (Dhiman and Prabhakar, 2020), which nowadays allows the production of massive amounts of micro- and nano-particles employing inexpensive and sustainable processes with less energy costs (Vilardi et al., 2017). One of the most attractive prospect is the possibility to micronize and apply in soil improvement activities the same materials/soil found on site with remarkable advantages from environmental point of view i.e. recycling and reuse of materials, better integration between engineering work and environment, reduction of CO_2 emissions from cement production cycle, materials transportation, etc. (Bavasso et al., 2016).
The advantage in using nanomaterials can be related to their particular structure: due to their very small dimension, nanomaterials develop an extremely large specific surface (Majeed and Taha, 2013) and have different properties compared with bulk materials from a physical and chemical point of view (Jeevanandam et al., 2018). Even if doesn't exist a single internationally accepted definition for nanomaterials, according to the EU Commission (2011) can be defined "nanomaterial" a manufactured or natural material that possesses for at least 50% unbound, aggregated or agglomerated particles where at least one external dimension is between 1-100 nm size range. These features allow nanomaterial's use as innovative materials in a large number of industries as medical, pharmaceutical, mechanical, chemical and civil engineering (Bavasso, 2018). About civil engineering applications, soil improvement is a challenging research topic continuously developing around technological innovation concerning materials and technologies.
The aim of soil improvement activities is to obtain a variation of the physical, hydraulic, and mechanical properties of soil, i.e. an increase of soil shear strength or a reduction of soil permeability, to meet specific engineering requirements (Behnood, 2018). The main advantages related to these techniques are the exploitation of marginal or polluted areas for new constructions, the provision of existent buildings' stability and the mitigation of the impact of undesired natural occurrence (i.e. earthquake, landslide, flood, etc.) and

anthropic ones (i.e. collapse phenomenon during mining activities, settlements during tunnelling or underground excavations, etc.).
Numerous methods are currently applied for this purpose based on their technological features. Low-pressure injection is one of the most used techniques and consists in substitution of pores and vacuums in the soil with materials mix injected with a valved tube. This method has specific advantages related to the possibility to operate in a confined area at a determined depth.
The materials normally used as mix components are clay, cement (Bahamani et al., 2014), microcement and nanocement (Ghasabkolaei et al., 2017), synthetic resin or a mixture of these elements, but recent studies also report the use of nanomaterials like nano-oxides i.e. alumina (Luo et al., 2012), copper oxide (Ghasabkolaei et al., 2017) and magnesium oxide (Majeed and Taha, 2012); natural nanomaterials i.e. clay (Majeed and Taha, 2012), bentonite (Shahin et al., 2015), silica (Proia et al., 2017), carbon nanotubes and soils (Ghasabkolaei et al., 2017); and even recycled nanomaterials i.e. sewage sludge ash (Luo et al., 2012), polyester fiber (Changizi and Haddad, 2015), flyash (Sachin Prabhu et al., 2017).
This contribution presents some preliminary results of a research activities developed to define the effect of natural based micro- and nano-materials in low-pressure injection for geotechnical soil improvement purposes, pointing out the effectiveness of the injection in the decrease of permeability in coarse-grained soils. The hydraulic aspect is, in fact, a relevant issue for countless applications as, among the others, dam, riverbank, , landfill stabilization, realization of horizontal and vertical barrier for pollutant containment, etc.
To reach the aforementioned aim, a first step was the characterization of micro-, nano-materials and sand used as well as the definition of the laboratory standards for the specimen creation in order to simulate the injection of mixture into the soil and to obtain treated soil samples as close as possible to the in situ conditions. Finally, constant head tests were carried out to provide hydraulic conductivity estimations.

2. Methodology

2.1 Materials

Materials used in this work to create the mixture were London clay, sand from Colleferro and graphene. Monogranular sand from Colleferro (described also in Guida et al., 2019) was also used as matrix to compose the samples. Materials granulometric range are showed in Table 1.

Table 1: Materials granulometric range

	Material	Dimension
Matrix	Sand	1÷2 mm
Mix	Sand	0÷100 μm
Mix	Clay	0÷100 μm
Mix	Graphene	0÷100 nm

The first step was the nano and micromaterials characterization in four substantial aspects: grains dimension (d_{50}), soil grains specific gravity (γ_s), Atterberg limits (w_L, w_P, IP) and mineralogical composition. These analysis was conducted on all materials except for graphene, due to its well-known characteristics. The results will be presented in paragraph 3.1, where d_{50} was obtained from granulometric analysis with sieves and hydrometer method adding sodium hexametaphosphate as dispersant in fine fractions (AGI, 1994); γ_s was obtained from helium pycnometer (ASTM D 854 - 92); w_L, w_P, IP were obtained from standard test methods (ASTM D 4318 – 17); mineralogy was acquired with an X-ray diffraction analysis.

2.2 Laboratory tests

Constant head permeability tests was performed in a triaxial cell (AGI, 1990) instead of a traditional permeameter in attempt to applying stabilization pressure ensuring that the filtration process takes place inside specimen.
Every test was carried out with cell pressure of 100 kPa and back-pressure of 50 kPa.
Testing program, showed in Table 2, consisted in 1 to 4 tests conducted for each sample (one untreated sample and one per mixture).

Table 2: Testing program

Mix	-	1A	1B	1C	2A	2B	2C	3A	3B	4A	4B
Number of tests	1	2	2	2	2	2	4	2	3	1	2

As a result, 24 constant head tests in triaxial cell were carried out.

2.3 Mix design and samples preparation

Four mixtures were defined based on their constituent elements in three different dilution rates.
In Table 3 is reported each mixtures composition.

Table 3: Mixtures composition

	Sand	Clay	Graphene	Water
	(%)	(%)	(%)	(%)
1A	35.3	21.2	1.1	42.4
1B	17.7	10.6	0.5	71.2
1C	26.5	15.9	0.8	56.8
2A	35.9	21.7	-	42.4
2B	17.9	10.9	-	71.2
2C	26.9	16.3	-	56.8
3A	56.5	-	1.1	42.4
3B	28.3	-	0.5	71.2
4A	-	56.5	1.1	42.4
4B	-	28.3	0.5	71.2

In order to prepare the samples, two injection modalities were adopted: one for denser mixtures (A and C typologies) and another for more diluted one (B typology). The first modality consisted in adding at the same time A or C mix and matrix in a mould, then placing it, after removing the stiff casing, in a latex membrane with fine sand inside. The choice of surrounding the sample with fine material was taken to hasten the drying process. A plastic small net was inserted between sample and fine sand to avoid contamination. The second modality consisted in pouring mixture directly in the monogranular sand matrix prepared inside the latex membrane and surrounded with fine sand like the previous way. Two samples set up with the modalities just explained are represented in Figure 1.

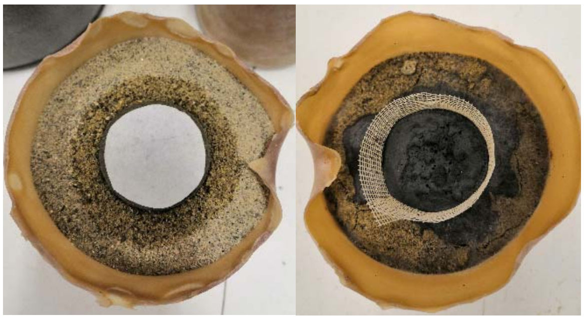

Figure 1: First (a) and second (b) injection modalities

3. Results

3.1 Characterization

Characterization results are showed in Table 4, Table 5 and Table 6 according to modalities expressed in the previous paragraph 2.1. London clay mineralogy is reported from literature (Burnett and Fookes, 1974).

Table 4: Characterization results

	Material	d_{50}	γ_S	w_L	w_P	IP
	(-)	(mm)	(kN/m^3)	(%)	(%)	(%)
Matrix	Sand	0.910	26.54	-	-	-
Mix	Sand	0.031	26.97	-	-	-
Mix	Clay	0.007	26.44	53.05	22.18	30.87

Table 5: Sand mineralogic analysis

Mineral	(-)	Calcite	Quartz	Albite	Phengite	Leucite	Aragonite	Dolomite
Quantity	(%)	36.26	29.67	17.21	10.19	3.30	2.09	1.25

Table 6: London clay mineralogic analysis (Burnett and Fookes, 1974)

Mineral	(-)	Quartz	Illite	Kaolinite	Felspar	Montmorillonite	Pyrite	Carbonate
Quantity	(%)	42.00	23.00	12.00	9.00	7.00	3.50	3.50

3.2 Permeability test

Constant head permeability test results are presented in Table 7. At first was analyzed hydraulic conductivity of an untreated sample, composed by only sand with granulometric range of 1÷2 mm, then all the other samples treated with nanomaterials mixtures.

Table 7: Permeability test results

	Permeability, k (m/s)				
	Test 1	Test 2	Test 3	Test 4	Mean Value
-	$9.4 \cdot 10^{-6}$	-	-	-	$9.40 \cdot 10^{-6}$
1A	$2.8 \cdot 10^{-7}$	$5.7 \cdot 10^{-7}$	-	-	$4.24 \cdot 10^{-7}$
1B	$2.3 \cdot 10^{-6}$	$1.4 \cdot 10^{-6}$	-	-	$1.87 \cdot 10^{-6}$
1C	$1.4 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$	-	-	$1.27 \cdot 10^{-6}$
2A	$5.7 \cdot 10^{-7}$	$4.2 \cdot 10^{-7}$	-	-	$4.95 \cdot 10^{-7}$
2B	$9.9 \cdot 10^{-7}$	$7.1 \cdot 10^{-7}$	$7.1 \cdot 10^{-7}$	-	$8.02 \cdot 10^{-7}$
2C	$2.8 \cdot 10^{-6}$	$1.4 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$	$9.9 \cdot 10^{-7}$	$1.63 \cdot 10^{-6}$
3A	$2.8 \cdot 10^{-7}$	$4.2 \cdot 10^{-6}$	-	-	$3.50 \cdot 10^{-7}$
3B	$1.1 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$	$8.5 \cdot 10^{-7}$	-	$1.04 \cdot 10^{-6}$
4A	$2.8 \cdot 10^{-7}$	-	-	-	$2.83 \cdot 10^{-7}$
4B	$1.3 \cdot 10^{-6}$	$8.5 \cdot 10^{-7}$	-	-	$1.06 \cdot 10^{-6}$

The next bar chart (Figure 2) illustrates the hydraulic conductivity values comparing untreated sand and other samples treated with nanomaterials mixtures.

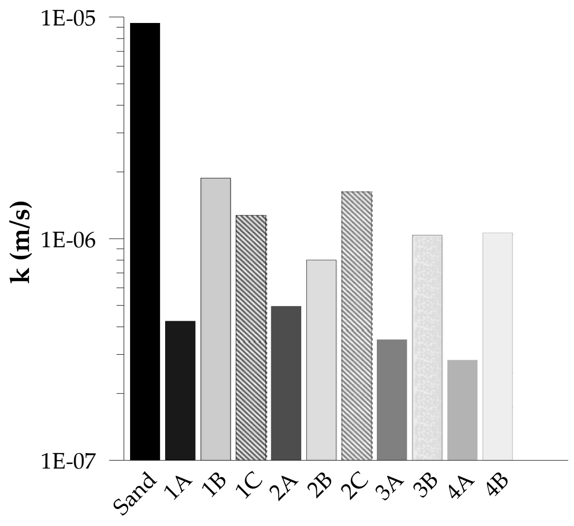

Figure 2: Hydraulic conductivity values for each mix and untreated sand

4. Discussion

In Figure 3 is illustrated the relationship between permeability and d_{10}. It was decided to correlate this grains dimension parameter with permeability because of the extremely similarity between d_{50} values in each sample.

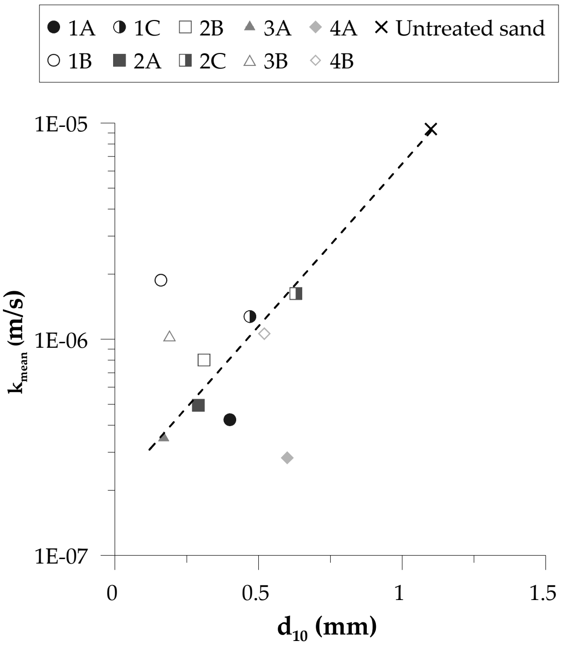

Figure 3: Correlation between permeability and d_{10}

It is possible from both Figure 2 and Figure 3 to notice the effectiveness of the treatment with nanomaterials in permeability reduction: each sample reports a decrease in hydraulic conductivity compared to the untreated sand.
The reason of permeability reduction is primarily due to pores and vacuums occlusion during micro- and nano-materials addition due to their smaller dimension, for these reasons most of the results seems aligned in a trend (Figure 3) in which the increase of the d_{10} is related to an increase of permeability. In support of this thesis, it appears that denser mixtures (1A, 2A, 3A, 4A) present lower permeability values associated with higher nanomaterials weight percent. Same results cannot be observed in B and C mixtures, where differences in permeability are not significant.
Furthermore, results seem to point out that the presence of graphene (1A, 3A, 4A mixtures) produces greater permeability reduction in comparison with its absence (2A mix). Evidences show that graphene doesn't cause the same decrease in lower density mixtures, probably due to the small amount of graphene compared with other components. It is possible that below a certain fixed dilution rate the contribution of graphene is negligible.
This attitude can be seen comparing 1 and 2 mixtures which differ in graphene presence: in samples injected with A (1A, 2A) and C (1C, 2C) mixtures, it can be observed that 1A and 1C present lower permeability compared with 2A and 2C. As mentioned earlier, same results can't be found in B mixtures where graphene percent is infinitesimal.
Unfortunately, other correlation between mixtures components and permeability can't be found; this confirm, as anticipated, that hydraulic conductivity decrease is caused mainly by increase in nanoparticles' content.

5. Conclusion and future development

In this paper, results from constant head permeability tests carried out on sand samples treated with nanomaterials are presented. Nano and micromaterials used in this work are London clay, sand from Colleferro and graphene. After materials characterization, four mixtures with three dilution rates were created and injected in the monogranular sand with two different modalities in order to reproduce conditions as close as possible to the site.
In summary, according to previous studies, this work proves that permeability reduction of 1 order of magnitude is reached due to natural-based nanomaterials injection. Permeability decrease is mostly correlated with density increase and presence of graphene in nanomaterials mixtures.
These preliminary evidences represent a new approach to low-pressure injection for soil stabilization, confirming the effectiveness of natural-based nanomaterials as mixture components. This could lead to an alternative and more sustainable solution with noticeable advantages from both environmental and economic point of view.

Finally, the following aspects should be explored in future research activities:

- role of viscosity on treatment effectiveness to improve workability;
- more extensive analysis of graphene effect, especially focused on interaction between matrix particles and other nanoparticles in mixture;
- investigate scale effect that can exist between laboratory and field through setting up field test.

References

Associazione Geotecnica Italiana, "Raccomandazioni sulla programmazione ed esecuzione delle indagini geotecniche", 1994.

Associazione Geotecnica Italiana, "Raccomandazioni sulle prove geotecniche di laboratorio", 1990.

American Society for Testing and Materials, "Standard Test Method for Specific Gravity of Soil Solids by Gas Pycnometer (ASTM D 854 - 92)", 1992.

American Society for Testing and Materials, "Standard Test Methods for Liquid Limit, Plastic Limit, and Plasticity Index of Soils (ASTM D 4318 – 17)", 2017.

Bahmani S. H., Huat B. B. K., Asadi A., Farzadnia N., "Stabilization of residual soil using SiO_2 nanoparticles and cement", Construction and Building Materials, 2014.

Bavasso I., Vilardi G., Stoller M., Chianese A., Di Palma L., "Perspectives in nanotechnology based innovative applications for the environment", Chemical Engineering Transactions, 2016.

Bavasso I., Verdone N., Di Palma L., "Cr(VI) Removal by Green-Synthetized Iron-Based Nanoparticles: Effect of Cr(VI) Concentration and pH Condition on Adsorption Process", Chemical Engineering Transactions, 2018.

Behnood A., "Soil and clay stabilization with calcium- and non-calcium-based additives: A state-of-the-art review of challenges, approaches and techniques", Transportation Geotechnics, 2018.

Burnett A. D., Fookes P. G., "A regional engineering geological study of the London clay in the London and Hampshire basins", 1974.

Changizi F., Haddad A., "Strength properties of soft clay treated with mixture of nano-SiO_2 and recycled polyester fiber", Journal of Rock Mechanics and Geotechnical Engineering, 2015.

Dhiman A., Prabhakar P. K., "Micronization in food processing: A comprehensive review of mechanistic approach, physicochemical, functional properties and self-stability of micronized food materials", Journal of Food Engineering, 2020.

Ghasabkolaei N., Choobbasti A. J., Roshan N., Ghasemi S. E., "Geotechnical properties of the soils modified with nanomaterials: A comprehensive review", ScienceDirect, 2017.

Guida G., Sebastiani D., Casini F., Miliziano S., "Grain morphology and strength dilatancy of sands",. Géotechnique Letters, 9(4), 245-253, 2019.

Jeevandam J., Barhoum A., Chan Y. S., Dufresne A., Danquah M. K., "Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations", Beilstein Journal of Nanotechnology, 2018.

Luo H. L., Hsiao D. H., Lin D. F., Lin C. K., "Cohesive Soil Stabilized Using Sewage Sludge Ash/Cement and Nano Aluminum Oxide", International Journal of Transportation Science and Technology, 2012.

Majeed Z. H., Taha M. R., "Effect of nanomaterial treatment on geotechnical properties of Penang soft soil", Engineering Geology, 2012.

Prabhu P. S., Prabu T., Eswaramoorthi P., "Influence of nanosized flyash and cement particles on the behaviour of soil", International Journal of Civil Engineering and Technology, 2017.

Proia R., Salvatore E., Mascolo M. C., Modoni G., "Miglioramento delle sabbie con aggiunta di nanomateriali", 2017.

Shahin S. S., Fayed L. A. E. M., Ahmad H., "Review of Nano additives in stabilization of Soil", 2015.

Vilardi G., Stoller M., Verdone N., Di Palma L., "Production of nano zero valent iron particles by means of a spinning disk reactor", Chemical Engineering Transactions, 2017.