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Technical Note

Effect of nanoparticles on the shrinkage properties of clay

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ABSTRACT

This study evaluates the effect of nanoparticles on the desiccation induced shrinkage of clay mixed with two different nanoparticles (i.e., nano-CuO and γ-Al_2O_3). The soil specimens were prepared by adding different amount of nanoparticles (i.e., 2%, 4% and 6% by weight) to a dry kaolin clay powder then water was added equal to the liquid limit. The shrinkage tests were carried out following the ASTM standard D4943 and the microstructure of the specimens was analyzed by scanning electron microscopy (SEM). The correlation between different percentages of nanoparticle amended clay was also analyzed by one-way analysis of variance (ANOVA) followed by the Tukey's honestly significant difference (HSD) test. The measurements suggest that addition of 6% nano-CuO and γ-Al_2O_3 increases the shrinkage limit of clay by 17% and 8%, respectively ($p < 0.05$). A low shrinkage limit is usually associated with large volume change. SEM images show that addition of nanoparticles in clay leads to a more flocculated fabric and thus leads to a higher shrinkage limit. With adding of 2% nanoparticles, decrease in the total volume reduction (Δv_{TOTAL}) of amended clay specimens is about 10% (8.75 cm^3; $p < 0.05$) and 6% (9.14 cm^3; $p < 0.05$), for nano-CuO and γ-Al_2O_3, respectively. However, the magnitude of Δv_{TOTAL} progressively diminishes with increasing nanoparticle percentage. These materials have the potential to be used as soil additives where desiccation induced soil shrinkage is severe.

1. Introduction

Compacted clays are commonly used as hydraulic barriers in waste containment facilities such as landfill covers. However, these compacted clays, subjected to seasonal drying by the Sun. and wind; and/or root water uptake by trees, can be desiccated. Desiccation causes the clay to shrink and eventually induces cracks that can undesirably increase the hydraulic conductivity of the clay cover. According the Albright et al. (2006), who carried out in-situ and laboratory permeability test of landfill covers with compacted clays, it is reported that hydraulic conductivity of compacted clays increased by three orders of magnitude after 4 years of service due to desiccation cracks. Many efforts have been made to overcome the negative effects of desiccation induced shrinkage in soils. One of the methods to reduce shrinkage is by utilizing additives such as sand, lime and fibers (Omidi et al., 1996; Miller and Rifai, 2004; Xue et al., 2014). Although soil shrinkage can be reduced by adding these additives, hydraulic conductivity is also increased. This increase in hydraulic conductivity can result in unfavorable conditions for slope stability and landfill covers, for examples. In recent years, the utilization of nanoparticles has gained increasing attention in a variety of applications. To give a few examples, nanoparticles are used in tires, sunscreens and will be increasingly used in medicines. Nanoparticles have also been used for increasing the strength of concrete (Amin and Abu el-hassan, 2015), remediation of contaminated groundwater (Tosco et al., 2014) and also soil remediation (Cundy et al., 2008). However, the use of nanomaterial as a soil additive is not that common yet.

Nanoparticles are considered as the building blocks for nanotechnology, and are referred to particles with at least one dimension <100 nm (Biswas and Wu, 2005). Baird and Walz (2005) studied the effects of silica nanoparticles on the structure of aqueous kaolinite suspensions. Stabilization/coagulation of kaolinite suspension was observed only when nanoparticles were added. Pham and Nguyen (2014) have also concluded that nanoparticles were able to inhibit montmorillonite swelling. Iranpour and Haddad (2016) have shown that nanoparticles were able to reduce the collapse potential of soil. Moreover, several studies have shown that a reduction in hydraulic conductivity can be achieved by mixing nanoparticles with soil (Kananizadeh et al., 2011; Ng and Coo, 2015; Taha and Taha, 2016), contrast to those previously reported additives. However, current understanding and test data related to the desiccation shrinkage behavior of nanoparticle amended soil are very limited. More quantitative studies are necessary to comprehensively understand the shrinkage characteristics of nanoparticle amended clay.

The shrinkage limit acquired from shrinkage tests is vital for engineers to assess the shrinkage potential of soil. The shrinkage limit is conceptually known as the boundary between “solid” and “semi-solid” consistency, and is defined as the water content at which the soil volume does not decrease even though the soil water content continues to decrease. Shrinkage tests also provide the shrinkage curve which is the volumetric shrinkage of soil specimens with a decrease in the

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water content during the shrinkage process. This shrinkage curve is a useful mean to understand shrinkage process and assist engineer to predict shrinkage induced volume change in soil. Knowledge of the shrinkage and desaturation properties is essential for improving assessments of soil strength and deformation as well as making advancement in the seepage analyses of unsaturated soils (Umezaki and Kawamura, 2013).

This study aims to investigate the effect of two nanoparticle types on the desiccation shrinkage behavior of clay. A series of shrinkage tests were carried out by preparing slurry specimens of pure kaolin clay and clay with different amounts of nanoparticles. The microstructure of the specimens was then analyzed by scanning electron microscopy (SEM). The correlation between different percentages of nanoparticle amended clay was analyzed by one-way analysis of variance (ANOVA) followed by the Tukey's honestly significant difference (HSD) test.

2. Materials and testing procedure

2.1. Soil and nanomaterials

The soil used in this study was kaolin clay which is classified as CH by the Unified Soil Classification System (USCS). Table 1 summarizes the basic properties of the clay. According to the findings of Benson et al. (1999), the geotechnical properties of the selected kaolin clay fall within the typical range of fine-grained soils utilized as landfill barriers. The two nanoparticles used in this study were nano-copper oxide (CuO) and gamma-aluminum oxide powder (γ-Al_2O_3), both with purity of 99.9% in dry powder form. Nano-copper oxide was a black powder with particle density of about 0.79 g/cm^3, average particle size of 40 nm and surface area at about 14 m^2/g. Gamma-aluminum oxide powder is a white to off-white powder, with particle density of about 3.6 g/cm^3, average particle size of 20 nm and surface area >180 m^2/g. The main basis for their selection is that both nanoparticles are insoluble in water and considered chemically stable. Taha and Taha (2012) conducted X-ray diffraction (XRD) tests and concluded that γ-Al_2O_3 did not chemically interact with soil by just mixing with water. Roy et al. (2015) also observed similar finding by mixing nano-CuO and kaolin clay with deionized water. Furthermore, CuO is considered chemically stable at ambient temperature to 300 °C (EPRI, 1999) and may only interact with kaolin at temperature of about 900 °C (Martišius and Giraitis, 2003). Another reason for the selection of these nanoparticles is due to the distinct differences in particle size.

2.2. Specimen preparation

Soil specimens were prepared by adding different amount of nanoparticles (i.e., 2%, 4% and 6% by weight) to a dry clay powder and mixed thoroughly before deionized water was added to achieve the required water content. All the dry soil specimens (i.e., pure kaolin clay and nanoparticle amended clay) were mixed with identical initial water content which is equal to the liquid limit of kaolin clay (see Table 1). The soil specimens were then compacted in accordance with the ASTM Standard Test Method for Shrinkage Factors of Soil by the Wax Method (ASTM D4943-08, 2008). Soil slurry equal to about one-third the volume of a shrinkage dish (40 mm in diameter and 12 mm in depth) was placed in the center of a dish. To allow the soil slurry to flow to the edges, the shrinkage dish was tapped several times on a firm surface. The process was repeated until the dish was filled. Any excess soil was then stroked off with a straightedge. Tapping of the soil slurry by layers ensured thorough and uniform compaction as well as removal of any entrapped air bubbles. For the pure clay and each percentage of nanoparticle amended clay, 140 specimens in total were prepared to obtain the desiccation induced volumetric shrinkage at different water content and for the sake of reproducibility. The associated index properties of pure clay and nanoparticle (i.e., nano-CuO and γ-Al_2O_3) amended clay are shown in Table 2.

2.3. Shrinkage tests

The specimens for the pure clay and each percentage of nanoparticle amended clay were air dried in a temperature (22 ± 2 °C) and humidity (53 ± 7%) controlled room. The shrinkage curve was also determined in accordance with the ASTM Standard Test Method for Shrinkage Factors of Soils by the Wax Method (ASTM D4943-08, 2008). To obtain the change in volume, the volume of selected specimens at different drying intervals was determined using the water displacement method. Each specimen was coated with molten wax of known density. Water displacement method was then used to determine the volume of the soil. This was repeated at intervals to establish the shrinkage path.

The reduction in volume of the specimens in a shrinkage test was determined from the volume-mass relationships by knowing the total mass and the volume of the wax coated specimen, the mass of the soil specimen, the mass and the volume of the wax, the initial water content of the soil specimen and the density of the wax. Lastly, the reduction in volume (Δv) calculates the void ratio and water content of the specimen at any stage of drying from the relations (Mishra et al., 2008):

$$\frac{\Delta v}{V_o} = \frac{\Delta e}{1 + e_o} \quad (1)$$

$$w = w_o - \frac{\Delta m}{m_s} \quad (2)$$

where V_o, e_o and w_o are the volume, void ratio and water content of the specimen at initial state; Δm, Δv and Δe represent the reduction in the weight, soil volume and void ratio at any stage of drying; m_s is the weight of soil solids and w is the gravimetric water content of the specimen at any stage of drying. It is noted that the focus of this study is to investigate the fundamental soil behavior of nanoparticle amended clay in terms of shrinkage properties during desiccation.

2.4. Scanning electron microscopy (SEM) imaging

Scanning electron microscopy provides direct observations on the fabric association in pure clay and nano-CuO amended clay. Specimens were carefully trimmed into a small cube with dimensions of ~5 mm.

Table 1
Basic properties of the clay.

Property	Value
Unified soil classification system	CH
Specific gravity, G_s	2.52
Atterberg limits	
Liquid limit, LL	70
Plastic limit, PL	33
Plasticity index, PI	37
Standard compaction curve	
Maximum dry density, ρ_d (kg/m^3)	1264
Optimum moisture content (%)	36.18
Saturated water permeability, k_s (m/s)	1.1×10^{-9}

Table 2
Index properties of the tested specimens.

Property	Value						
	Kaolin clay	Clay-nanomaterial mixture Material added: wt%					
		nano-CuO			γ-Al_2O_3		
		2%	4%	6%	2%	4%	6%
Liquid limit, LL	70.1	72.3	70.8	66.8	74.8	79.9	82.3
Plasticity index, PI	37.0	38.9	35.5	30.2	37.7	37.5	34.7