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Effects of nano-kaolinite clay on the freeze–thaw resistance of concrete

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ABSTRACT

This paper investigates the effects of nano-kaolinite clay (NKC) on the freezing and thawing (F–T) behavior of concrete. In our experiments, we substituted NKC for 0%, 1%, 3%, and 5% of mixtures of ordinary Portland, cement, by weight. The blended concrete was prepared using w/c ratio as 0.5. A rapid freeze–thaw Cabinet was then used to measure the resistance of ordinary Portland cement concrete, as opposed to the concrete/NKC mixture, to examine deterioration caused by repeated F–T actions. We regularly measured the properties of the concrete specimens, including the pore structure, mass, electrical resistivity, chloride diffusion coefficient, compressive strength and dynamic modulus of elasticity. A computed tomography scan test evaluated the porosity characteristics of the concrete. This paper also applied scanning electron microscopy and X-ray diffraction tests in order to investigate the micro morphology and chemical element distributions inside of the concrete. The experimental results and visual comparisons revealed that the introduction of NKC improves the F–T resistivity values, as compared to the control concrete. The samples with 5% NKC exhibited the highest compressive strength, chloride diffusion resistivity, relative dynamic modulus of elasticity, and the most electrical resistivity after 125 F–T cycles. We designated the anti-freezing durability coefficient (DF) as the index to assess the F–T resistivity of concrete. The following research discusses the relationship between the concrete's DF and the number of F–T cycles, compressive strength, chloride diffusion coefficient, and the electrical resistivity of the concrete samples.

1. Introduction

Worldwide, innumerable concrete structures are in need of repair, due to exposure to severe winter conditions. Freeze–thaw (F–T) durability of concrete is a crucial factor that affects the durability of these concrete structures in cold regions. Many theories related to the action of frost on concrete (including osmotic pressure theory, classic hydraulic pressure theory, crystallization pressure theory, and others) have been put forward over the last 60 years [1].

Concrete is inherently a porous material. The F–T resistance of concrete depends on the structure of the material, namely its porosity, the size of its pores and capillaries, their distribution across the material, and the type of pores (open or closed) [2–6]. To protect concrete from F–T damage, a number of researchers have studied the factors affecting the material performance of concrete exposed to F–T actions. Experimental data from both laboratory and field tests has shown that well-distributed air voids can provide pressure release and improve freezing and thawing resistance [7]. Therefore, the life of concrete structures will be greatly increased once less permeable concrete is produced. Some researches reported that the addition of additives, such as fly ash, silica fume, ground granulated blast furnace slag, rice husk ash, and polypropylene fibers, in concrete can improve both its permeability and freeze–thaw resistance [8–15]. However, some studies gave the contradictory results [16–18]. In recent years, several studies reported that the addition of nanomaterials could reduce concrete's permeability to fluids and control calcium leaching [19–35]. The results show that adding kaolinite clay (1% by mass of cement) is effective way to improve the chloride resistance of concrete [36–40]. Research indicates that the introduction of 1–3% nanoclay results in even higher compressive strength, lower permeability, and higher acid resistance within concrete structures. It is anticipated that using nanoclay may increase the F–T resistance of cement concrete. Despite recent attention to the performance of nanoparticle additions in cementitious materials, little information exists related to the behavior of nanoclay-modified concrete, when exposed to F–T actions.

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The objective of the study is to analyze the effects of nanokaolinite clay (NKC) in concrete subjected to F–T actions. We conducted experiments to determine the F–T durability of concrete containing 1%, 3%, and 5% NKC, using the rapid F–T method. Tests on physical pore characteristic, mechanical property, permeability, and electrical conductivity were conducted on concrete with and without NKC particles that were subjected to F–T cycles. Furthermore, we characterized the microstructure of cement concrete using SEM, EDS, and XRD in order to evaluate the effects of NKC particles on the improved strength and decreased permeability of concrete. By knowing the concrete's base behavior during the freezing and thawing process, it is possible to identify the benefits caused by the addition of NKC particles. These results can help to better inform architectural designs and maintenance for concrete structures, by taking the F–T durability of NKC-modified concrete into consideration.

2. Experimental study

2.1. Material properties

This study utilizes ordinary Portland cement, type 42.5R, and commercially available NKC powder. NKC has a crystalline structure and contains silicon, whose theoretical formula is $Al_2Si_2O_5(OH)_4$ [41]. The chemical compositions of the cement and clay are listed in Table 1. The properties of NKC used in this study are listed in Table 2. To characterize the chemical and microstructure of the NKC studied in this paper, X-ray diffraction (XRD) analysis and Transmission electron microscopy (TEM) techniques were carried out on the clay powder. The resulting TEM and XRD images of the clay powder samples are shown in Fig. 1. Based on the micrograph of NKC powder, the particle size distribution of the powder is analyzed and plotted in Fig. 1c. We obtained the elemental composition of the NKC power samples from the EDS spectra, as listed in Table 3.

2.2. Specimen preparation

The mass ratio of cement: water: sand: aggregate in this study's concrete mixture is 350: 175: 619: 1256, respectively. The effective dispersion of NKC throughout the concrete mixture is critical to achieving full benefits. Based on previous studies, the NKC was first dispersed in water using an ultrasonic dispersion method [37]. Then, the dispersed clays were mixed with fine and coarse aggregate following the JTG E30-2005 [42]. The mixed concrete was then poured into oiled molds to form prisms, sized 100 mm × 100 mm × 400 mm, which were used for the F–T tests. The fabricated samples were demolded after 24 h and were then cured using standard curing conditions (the temperature is 20 °C ± 2 °C and the relative humidity is over 95% RH). Three specimens were created in the control group (ordinary Portland cement concrete with no clay added) and the clay-modified concrete. To investigate the effects of clay additives on concrete's properties we studied clay-modified concrete mixtures with 1%, 3%, and 5% NKC by mass. The control concrete specimen and the concrete containing 1%, 3%, and 5% NKC additives were denoted as NC0, NC1, NC3, and NC5, respectively.

Table 1
Chemical composition of cement.

Chemical components	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3
Content (%)	59.30	21.91	6.27	3.78	1.64	2.41

Table 2
Physical index of nano-kaolinite clay.

Average flake diameter (nm)	Average flake thickness (nm)	Specific surface area (m^2/g)	Density (g/cm^3)
300–500	20–50	30	0.6

2.3. Methods

The Rapid Freeze–Thaw Cabinet (see Fig. 2a), which satisfies the GBJ82-85 procedure requirements, was used to produce F–T cycles in water [43]. The F–T cycle consisted of alternatively lowering the temperature of the specimens from 4 to −18 °C and raising it from −18 to 4 °C in 3 h. The temperature curve of the F–T cycle is shown in Fig. 2(b).

At regular intervals of 25 F–T cycles, the samples are removed from the apparatus. We allowed the removed specimens to dry on the surface, and then performed physical, dynamic modulus, electrical resistivity, compressive strength, CT, SEM/EDS, and XRD tests. We compared our experimental results in order to explore the attributions of NKC on the properties of concrete.

2.3.1. SEM/EDS

To better understand the effects of NKC on the microstructure of the concrete samples, we conducted a microstructural morphology and elemental composition analysis on the plain concrete and NKC-modified concrete samples, using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). We extracted an ordinary Portland cement-based concrete specimen, with the dimension of 5 mm × 5 mm × 5 mm, from the central part of the concrete specimen. The prepared samples were then observed using the JSM-6360LV SEM system, and the intensity of the applied voltage is 20 kV. To make the samples conductive, the surface of the samples was coated with 10 nm thick gold. The same equipment was used to determine the morphology of the NKC-modified concrete, in order to compare it to the control concrete. 20 images were taken per samples.

2.3.2. X-ray power diffraction

Furthermore, a XRD analysis was conducted to discover the effects of the NKC addition to the growth of crystals in the concrete. The cubic samples with the dimensions of 1 cm × 1 cm × 1 cm were extracted from the central part of the concrete specimen. The prepared samples were examined using a Rigaku D/max-Ultima+ Powder XRD system. A measurable 2θ-range is from 10° to 90°, and the scan rate is 4°/min.

2.3.3. Pore characteristic

It is known that the F–T durability of concrete has close relationship with its pore structure. Within a certain temperature interval, concrete that contains more frozen pores induces greater internal hydraulic pressure and, consequently, more severe frost damage [6]. Therefore, in studying the behavior of NKC-modified concrete subjected to F–T actions, it is critical to assess the pores within the concrete. This investigation uses a 'Siemens somatom sensation' 16-slice spiral computed tomography scanner, which was made in Germany. The pore characteristics in the concrete samples (with the dimensions of 100 mm × 100 mm × 100 mm) were examined using a CT test after exposure to 0, 50, and 100 F–T cycles. The samples were scanned with a fixed X-ray source, at 140 kV, 200 mA, and 22.60 mGy CTD. The samples were scanned at 1 mm spacing, and 100 slices were obtained. The output scanning section of concrete is documented using the DCM format, and the CT number is stored in 12 digital capacities. The obtained